

GWERD QUALITY ASSURANCE PROJECT PLAN

Title: Hydraulic Fracturing Retrospective Case Study, Bakken Shale, Killdeer and Dunn County, ND

TASK No. 26278

QA ID No. G-16094

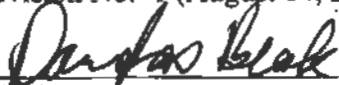
QA Category: 1

HF Project #14

Date Original QAPP submitted: April 15, 2011

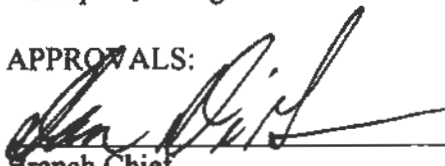
Number of Pages: 93

Revision No: 1 (August 14, 2011)


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1.0 Project Management

1.1 Project/Task Organization

The organizational structure for the Hydraulic Fracturing Retrospective Case Study located in the Bakken Shale, in Dunn county and near the city of Killdeer, ND is shown in Figure 1. The responsibilities of the principal personnel associated with this case study are listed below.

Dr. Douglas Beak, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Beak is the principal investigator of this project and is responsible for preparing and maintaining the QAPP and ensuring completion of all aspects of this QAPP, including overall responsibility for QA. He will lead the collection, analysis, and interpretation of groundwater and surface water samples. He is the Health and Safety Officer for groundwater and surface water sampling activities carried out by NRMRL-Ada. His HAZWOPER certification is current.

Dr. Robert Puls, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Dr. Puls is the Technical Research Lead for case studies. He is also assisting in the coordination of the Hydraulic Fracturing Study with the North Dakota Industrial Commission, Oil and Gas Division (NDIC) and North Dakota Department of Health, Division of Water Quality (NDDWQ).

Mr. Steve Vandegrift, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Vandegrift is responsible for quality assurance review/approval of the Quality Assurance Project Plan (QAPP), conducting audits, and QA review/approval of the final report. His HAZWOPER certification is current.

Mr. Russell Neill, Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OK. Mr. Neill is responsible for assisting in ground water sampling. His HAZWOPER certification is current.

Dr Randall Ross, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Dr. Ross will assist in the analysis of hydrologic conditions at the Killdeer site and will assist in the development of the site hydrologic conditions. His HAZWOPER certification is current.

Mr. Steve Acree, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. Acree will assist in the analysis of hydrologic conditions at the

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Killdeer site and will assist in the development of the site hydrologic conditions. His HAZWOPER certification is current.

Mr. Mark White, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Mr. White is responsible for overseeing sample analysis in the General Parameters Laboratory (anions, nutrients, organic and inorganic carbon).

Ms. Cherri Adair, U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center (RSKERC), Ada, OK. Ms. Adair is responsible for assisting Dr. Beak with health and safety issues related to the study. Her HAZWOPER certification is current.

Mr. Chris Ruybal, Student Contractor, Ada, OK. Mr Ruybal is responsible for assisting in ground water sampling. His HAZWOPER certification is current.

Mr. Gregory Oberley, U.S. Environmental Protection Agency – Region VIII, Denver, CO. Mr. Oberley is responsible for coordinating technical discussion and activities between NRMRL-Ada and EPA Region VIII and Region VIII Analytical Lab, as well as coordinating data collection activities with the state officials in North Dakota. He will also assist in ground water sampling. His HAZWOPER certification is current.

Dr. Mark Burkhardt, U.S. Environmental Protection Agency – Region VIII, Golden, CO. Dr. Burkhardt will be responsible for overseeing analysis of organic compounds in the Region VIII laboratory.

Dr. Sujith Kumar, Shaw Environmental, Ada, OK. Dr. Kumar is responsible for overseeing the analytical work performed under GWERD's on site analytical contract (VOC's, dissolved gases, and metals).

Ms. Shauna Bennett, Shaw Environmental, Ada, OK. Dr. Ms. Bennett is the QC Coordinator for Shaw Environmental and will coordinate QC for Shaw Environmental portion of this study.

Mr Kris Roberts, North Dakota Department of Health, Division of Water Quality. Mr. Roberts is the primary point of contact in North Dakota for site access and pre-existing data and data collected by Denbury's contractor Terracon.

Mr. Lynn Helms, North Dakota Industrial Commission, Department of Mineral Resources. Mr. Helms is a point of contact for oil and gas information.

Ms. Cynthia Caporale, USEPA Region 3 Analytical Laboratory, Laboratory Branch Chief/Technical Director. Ms. Caporale will act as a liason between the Region 3 Lab and RSKERC.

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Dr. Jennifer Gundersen, U.S. Environmental Protection Agency – Region III, Ft. Meade, MD. Dr. Gundersen will analyze samples for glycols.

Mr Ryan Jacob, Denbury Onshore, LLC. Mr. Jacob is the primary point of contact with Denbury and will assist in coordination of field sampling activities. Mr. Jacob will also act as the liason between Denbury and EPA as well as Terracon Consultants the onsite contractor.

Mr. Michael Bullock, Terracon Consultants. Mr Bullock is the point of contact inside of Terracon.

Dr. Zell Peterman, U.S. Geological Survey, Denver, CO. Dr. Peterman is responsible for the analysis of strontium isotope ratios.

Doug Beak is responsible for initiating contact with appropriate project participants as he deems necessary. Other project participants will keep Doug Beak informed whenever significant developments or changes occur. Lines of communication among project participants may be conducted via in person conversations, electronic mail, phone conversations, conference calls, Environmental Science Connector and periodic meetings.

1.2 Problem Definition/Background

The retrospective case study in the Bakkan Shale will investigate the potential impacts, if any, of a well blow out on drinking water resources in Dunn County, near Killdeer, ND. The investigation will initially involve sampling ground water, beginning July 2011, in the area surrounding the well pad, Franchuk 44-20SWH, near Killdeer ND. This study will be conducted in conjunction with the North Dakota Industrial Commission, Oil and Gas Division (NDIC); North Dakota Department of Health, Division of Water Quality (NDDWQ); U.S. Environmental Protection Agency, Region VIII (EPA R8); Denbury Onshore, LCC (Denbury); Terracon Consultants (Terracon); and U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecological Restoration Division (GWERD). GWERD will be the lead organization for this case study.

Killdeer, North Dakota (ND) is located in Dunn County in West Central ND and has an estimated population of 1000 individuals. The area surrounding Killdeer is currently experiencing renewed oil and natural gas exploration using horizontal drilling technology and hydraulic fracturing is being employed to stimulate production in these wells. In September, 2010 an oil well (Franchuk 44-20SWH, operated by Denbury) (Figures 2 and 3) near Killdeer experienced a uncontrolled blow out during the 5th stage of a 23 stage fracturing operation when the seven inch intermediate casing burst. This resulted in the spilling of approximately 2000 barrels (84,000 gallons) of hydraulic fracturing fluids (See Table 1 for known constituents) and oil on to the surface. At this time it is suspected that hydraulic fracturing fluids and oil were

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released into the subsurface because the surface casing was compromised at 38.5 ft below land surface and there is still a question about whether the conductor casing was compromised at 60 ft below land surface. During the clean up process approximately 1007 (42,294 gallons) barrels of water and 125 barrels (5250 gallons) of oil were recovered. To date it is unknown if groundwater contamination occurred and what the extent of the groundwater contamination might have been. The Franchuk well is just outside the City of Killdeer's Municipal Water Supply Wells, well head protection zone (~2.5 miles). In addition, there are several farm wells in the vicinity of the Franchuk well and supply wells for drilling and hydraulic fracturing activities is approximately 0.5 miles down gradient of the Franchuk well (Figure 3).

The Killdeer Aquifer is underlying the site and is the source of drinking water for the City of Killdeer, several domestic wells and also serves to supply water for drilling operations in the area. In addition, an intermittent creek meanders along sides of the drilling pad and is believed to be a recharge the Killdeer Aquifer (Figure 3). The aquifer is overlain by till and clay.

Four groundwater monitoring wells (MW1- MW4) were installed by Terracon in September, 2010 to monitor for potential groundwater contamination in the Killdeer Aquifer. An additional five monitoring wells (MW5- MW8D) were installed at the site in April, 2011. These wells were constructed using 2 in. diameter PVC and screening intervals are listed in Table 2 and shown in Figure 4.

The objectives of this case study are listed below.

Primary Objective: Evaluate if the Killdeer Aquifer was impacted by the blow out that occurred during hydraulic fracturing. (See Section 1.3)

Secondary Objective 1: Determine the mechanism(s) of how the Killdeer Aquifer was impacted if there was an impact. (See Section 1.3)

1.2.1 Phase I Investigations

In Phase I, selected domestic wells and monitoring wells as well as a North Dakota Water Commission well will be sampled with subsequent analyses to determine the nature of water contamination, if it exists. The wells selected for sampling are based on site investigation approved by the NDDWQ. If evidence of ground water or surface water contamination is indicated in Phase I sampling, Phase II activities will be targeted to confirm the initial result and to identify the source or sources of contamination. If no contamination is detected in the first Phase I screening event, it is anticipated that a limited follow-up sampling would take place to confirm the result. Water sampling for Phase I sampling is expected to take place in July 2011. Version 0 of this QAPP describes quality assurance and quality control procedures associated with water sampling for Phase I studies. Subsequent revision of the QAPP to include soil

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sampling and other activities, if appropriate, will occur following evaluation of Phase I results or whenever revisions are necessary.

1.2.2 Phase 2 Investigations

Phase II activities will likely involve additional ground-water sampling, monitoring well sampling, and may involve installation of temporary or permanent wells for hydrogeologic and geochemical characterization, and geophysical surveys. These will be used to further refine the site conceptual model and the types of sampling and methodology will be outlined in future revisions to the QAPP.

1.2.3 Integration of Phase 1 and 2 investigations and determination of impacts to drinking water resources

Multiple lines of evidence will be needed to arrive at conclusions concerning the sources of impacts to drinking water. Hydraulic fracturing chemicals and contaminants which can be mobilized from native geologic materials can have other sources (e.g., other industries and naturally present contaminants in shallow drinking water aquifers [e.g., As, U, Ra, Ba]). It will therefore be necessary to exclude other sources before assigning hydraulic fracturing operations responsibility for impacts to drinking water supplies. Some hydraulic fracturing chemicals are used in a host of different products and processes which could also find their way into drinking water supplies. Reactive transport models can be useful in supporting data from site assessments to support or refute conceptual models regarding exposure pathways and impacts. These same models can also help in assessing uncertainties associated with conclusions regarding the source of impacts.

1.3 Project/Task Description

In order to accomplish the primary objective listed in section 1.2, the existing monitoring wells network, the domestic wells, municipal supply wells, and the supply wells will be sampled (Figures 1, 2, 3) and analyzed for the components of crude oil: Gasoline Range Organics (GRO), Diesel Range Organics (DRO), volatile organic compounds (VOC), semivolatile organic compounds (SVOC) and dissolved gases (methane, ethane, propane, butane). In addition, well samples will be analyzed for glycols, barium (Ba), and select hydraulic fracturing fluids components (potassium (K), alcohols, naphthalene, and boron (B)), potentially mobilized naturally occurring substances (arsenic (As), selenium (Se), strontium (Sr), and other trace metals), and changes in background water quality (DOC, DIC major anions and cations). Of these target analytes, those that are critical analytes supporting this primary objective are delineated in Table 3. A tiered approach will be applied to the use of the glycol data. Initially, the data will be considered as "screening" data as the method is under development and is not yet validated. Once the method is validated, the glycol data will no longer be considered as

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“screening” data. A tiered approach will also be applied to the VOC and SVOC data. See footnote to Table 3.

In order to address secondary objective 1, groundwater sampling will be needed. The target parameters listed in the primary objective will be needed to address this objective.

It is anticipated that the data collected from this case study will be incorporated into the larger Hydraulic Fracturing report to congress. It is also anticipated that this data will be utilized in EPA reports, conference proceedings and journal articles. In addition, the data collected in this case study may be used in policy and regulation efforts in EPA and state regulatory agencies.

A proposed schedule for field activities is provided in Table 4.

1.4 Project Quality Objectives and Criteria

As part of this case study detailed site history (blow out event, hydrologic conditions and settings, Killdeer aquifer water quality data, monitoring well locations and construction, background geology data, soil data, and data collected on the extent of contamination as well as agricultural and industrial activities in the area) has been collected and is continuing to be collected. This data has been collected from the USGS and Terracon (on site contractor for Denbury Resources), NDIC and NDDWQ. The site history will be used to determine the background conditions at the site as well as the potential for other activities in the area to be a potential source of the impact to the Killdeer Aquifer. Natural sources of contaminants or other human activities could potentially create sample bias and effect the conclusions of the study.

The installed monitoring well network surrounding the Franchuk well should yield a representative data set that will address whether local contamination of the Killdeer aquifer occurred or if there is the potential for contamination in the future. To date EPA has received limited information on the hydrologic conditions near the well pad. We are currently relying on a monitoring well network installed by Denbury on site contractor, Terracon, and the NDIC and NDDWQ to adequately detect impacts near the well pad. During the initial and subsequent sampling events water level measurements will be taken and groundwater flow directions will be determined using standard techniques (Domenico and Schwartz, 1990) to determine: if the current monitoring network will address the primary objective of the study; are additional monitoring wells needed; and if additional monitoring wells are needed, at what locations should these wells be placed.

Other project quality objectives, such as precision, accuracy, sensitivity, and etc. will be discussed primarily in sections 2, 3, and 4.

1.5 Special Training/Certification

A current HAZWOPER certification is required for on-site work. HAZWOPER training and yearly refresher training is provided to GWERD personnel at an appropriate training facility

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chosen by GWERD SHEMA (Safety, Health, and Environmental Management Program) manager. The HAZWOPER certificate and wallet card is provided to each person completing the training.

The laboratories performing critical analyses in support of this case study must demonstrate their competency in the fields of analyses to be conducted, prior to performing such analyses. Competency may be demonstrated through documentation of certification/accreditation or some other means as determined to be acceptable by project participants. The EPA GP laboratory and the Shaw laboratories, the on-site contractor laboratory at RSKERC, will be used to analyze select critical analytes listed in Table 3. These laboratories have demonstrated competency through the implementation of ORD PPM 13.4, *Quality Assurance/Quality Control Practices for ORD Laboratories Conducting Research* which includes external independent assessments. These laboratories are also routinely subjected to internal laboratory assessments and performance evaluation (PE) samples.

The USEPA Region VIII Laboratory will be used to analyze those critical analytes listed in Table 3. . This laboratory has been subjected to the National Environmental Laboratory Accreditation Program (NELAP) accreditation process through the state of Texas and is expected to soon be granted approval.

The Region III Laboratory will be used to analyze glycols, which is not identified as critical at this time. However, it is accredited under the NELAP through the state of New Jersey as the Accrediting Body. The particular method being used by Region III for these analyses are not accredited, but the laboratory follows all the requirements for an accredited method. However, initial data reported from the glycol analysis will be flagged as "screening" data from a method that is currently being developed. Once the data is validated, it will no longer be flagged as "screening" data.

1.6 Documents and Records

Data reports will be provided electronically as Excel spreadsheets. Shaw's raw data is kept on-site at the GWERD and will be provided on CD/DVD to Doug Beak. Raw data for sub-contracted laboratories shall be included with the data reports. Calibration and QC data and results shall be included. Field notebooks will be kept as well as customized data entry forms if needed. All information needed to confirm final reported data will be included.

Records and documents expected to be produced include: field data, chain-of-custody (COC), QA audit reports for field and laboratory activities, data reports, raw data, calibration data, QC data, interim reports, and a final report.

All field and laboratory documentation shall provide enough detail to allow for reconstruction of events. Documentation practices shall adhere to ORD PPM 13.2, *Paper Laboratory Records*.

Since this is a QA Category 1 project, all project records require permanent retention per Agency Records Schedule 501, *Applied and Directed Scientific Research*. . They shall be stored

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in Doug Beak's office in the GWERD until they are transferred to GWERD's Records Storage Room. At an as yet to be determined time in the future the records will be transferred to a National Archive facility.

2.0 Data Generation and Acquisition

2.1 Sampling Process Design (Experimental Design)

First sampling event in July 2011 will not include surface water, soil and sediment. The QAPP will be revised prior to sampling events in which these will be included in the sampling.

2.1.1 Background Hydrological Information

The Killdeer aquifer (Figure 5) occupies an area of about 74 mi² (190 km²) in Dunn County. It extends southward to the Stark County line in the southeast corner. From this point the aquifer extends east along the northern edge of Stark County. The tributary channels extending northward from the Stark County are hydraulically connected to the aquifer in Stark County and are therefore considered to be part of the Killdeer aquifer (Klausing, 1979).

This aquifer composition is predominantly fine to medium sand. However several test holes indicate fine to coarse gravel near the base (Klausing, 1979). The maximum thickness is 233 ft (71 m) and the mean thickness of the aquifer is 80 ft (24 m) (Klausing, 1979). A geologic cross section of the aquifer near the Franchuk well is shown in Figure 5B. The aquifer is generally overlain by clay and silt soils (Klausing, 1979).

Klausing (1979) provides hydrologic data for the Killdeer aquifer. The transmissivity was determined to be approximately 10,000 ft² d⁻¹ (929 m² d⁻¹) and a storage coefficient of 0.02. Depending on the aquifer thickness and hydraulic conductivity the aquifer yield was estimated to range from 50 to 1000 gal min⁻¹ (11 to 3785 L min⁻¹). The aquifer is recharged by infiltration of precipitation and discharged naturally by base flow into Spring Creek, Knife River and by evapotranspiration. Water levels in the aquifer range from about 0.3 feet (0.09 m) above lsd to about 37 ft (11 m) below lsd. Seasonal fluctuations range from about 1 ft (0.3 m) to a maximum of about 7 ft (2 m). The minimum seasonal fluctuations occur in a confined part of the aquifer, whereas the maximum fluctuations occur in an unconfined part. Klausing (1979) estimated that the water potentially available in storage of the Killdeer aquifer is 568,000 acre-ft.

Klausing (1979) also reported on the water quality of the Killdeer aquifer (Table 5). In general the water is very hard and either a NaHCO₃ or NaSO₄ type water. In general the northern portion of the aquifer is of better quality than that of the south. The TDS in the northern portion rarely exceeds 1100 mg L⁻¹, but in the southern portion of the aquifer TDS commonly exceeds 2000 mg L⁻¹.

2.1.2 Installation of Monitoring Wells

Terracon (contracted by the well operator, Denbury Resources) was contracted for the installation of monitoring wells (Figure 4). The physical characteristics of the monitoring wells are provided in Table 2. According to the information provided by Terracon to the NDDWQ the groundwater flow direction is to the southwest and has relatively uniform gradient of 0.0009 ft ft⁻¹.

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¹ to 0.0008 ft ft⁻¹. Although the ground water flow direction and gradient could vary seasonally due to precipitation and water usage. The North Dakota State water commission stated that the ground water flow within the Killdeer aquifer is <1 ft day⁻¹.

The monitoring wells were constructed using 2 inch PVC casing and slotted PVC screens. The screen intervals in the monitoring wells were based on information generated as part of Terracon's investigatory activities of the groundwater and the damaged well casing. The annular space between the borehole wall and the well screen was backfilled with 10-20 silica sand, usually to two feet above and below the screened interval. The remaining annular space above the sand pack was sealed with bentonite. The wells are then completed at the surface by concreting a stick up protective monitoring well cover at MW7 and MW8 and using flush mounted covers at the surface between the bentonite backfill and concrete cap. The designated measuring point and elevation datum at each monitoring well is defined as the ground surface immediately adjacent to the surficial concrete seal to the north and the top of the PVC well casing on the north side. These points will be surveyed by Terracon in the horizontal and vertical positions of the monitoring wells at some point (Information provided by Terracon to the NDDWQ).

The installed wells were developed by Terracon and the procedure used is not known. Once the wells were developed the monitoring wells were fitted with dedicated bladder pumps.

2.1.3 Ground-Water Monitoring

The ground-water sampling component of this project is intended to provide a survey of water quality in the area of investigation. GWERD, EPA R8, and NDIC, NDDWQ will survey the existing data and potentially speak to landowners near the Franchuk well to determine if ground water wells in the area could be sampled for the study if additional groundwater sampling locations are needed. These monitoring wells will be made available to GWERD for sampling and sampling by the NDIC and NDDWQ. Monitoring wells were installed in locations where contamination is suspected based on data collected by NDIC and Terracon immediately after the spill and considering the hydrogeologic conditions at the site. In addition to the nine monitoring wells, three domestic wells, and four water supply wells used for drilling activities in the area will be sampled along with the City of Killdeers Municipal Supply wells. The locations of the domestic wells and water supply wells are shown in Figure 2. The domestic well(s), near the Franchuk location will be sampled via homeowner taps. It is believed that most domestic wells are screened in the Killdeer Aquifer between 30 and 200 ft below ground surface. Similarly, the water supply wells will be sampled similar to the domestic wells and are shown in Figure 2. The City of Killdeers Municipal wells are located within the City of Killdeer and are screened in the Killdeer aquifer (Figure 2). It is anticipated that the monitoring wells will be sampled approximately quarterly over a period of about one year (Table 4). The spacing of the ground-water sampling events will in part depend on weather conditions and also on when site access (during Terracon's quarterly sampling) can be obtained but is anticipated to start in July 2011 and continue through August 2012. The minimum number of sampling events to determine if an impact to the Killdeer aquifer happened is estimated to be three sampling events, but up to six

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are possible. The study area and locations of monitoring wells are illustrated in Figures 2, 3 and 4.

2.2 Sampling Methods

2.2.1 Ground-Water Sampling

Dedicated bladder pumps have been installed in the monitoring wells and will be used to sample water from these wells. The pump intake location within the screened interval is unknown at this time. Domestic wells, supply wells and municipal wells have dedicated pumps believed to be within the screened interval of the well and again this information is unknown at this time. This information will be collected in future as part of the ongoing site history investigation.

2.2.1.1 Monitoring wells

The following methodology will be used for the monitoring wells.

- 1) Water level measurements will be taken prior to pumping wells. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in the field notebook prior to sampling.
- 2) A new piece of tubing will be connected to the sampling port of the well and the dedicated pump will be powered on. It is expected that the pump will yield a maximum initial flow rate of approximately 1 L min⁻¹). This flow will pass through a flow cell equipped with an YSI 5600 multiparameter probe (or equivalent probes). The rate of pumping will be determined by measuring the water volume collected after approximately 15 seconds into a 4 L graduated cylinder; the desirable pumping rate through the flow cell should be less than 1 L/min. The pumping rate will ideally maintain minimal drawdown. Water levels will be taken following sampling to confirm the drawdown caused by pumping.
- 3) The YSI probe (or equivalent probes and electrodes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the guidelines in Table 6 will be used to determine when parameters have stabilized. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.
- 4) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded.
- 5) After the values for pH, ORP, SC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples will be collected as follows:

- a. Duplicate 40 mL VOA vials (amber glass) will be collected, without headspace, for VOC analysis using RSKSOP-299v1. Tribasic Sodium Phosphate (TSP) will be added to the VOA vial prior to shipping to the field for sampling as a preservative. (Acid will not be used as a preservative due to a concern of acid hydrolysis of some analytes.) The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for GC-MS analysis.
- b. Duplicate 60 mL serum bottles will be collected, without headspace, for dissolved gas analysis (e.g., hydrogen, carbon dioxide, ethane, methane, butane, propane). The bottles will contain trisodium phosphate as a preservative and will be filled with no head space and sealed with a crimp cap. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.
- c. Duplicate 1 L amber glass bottles will be collected for semi-volatile organic compounds. These samples will be stored and shipped on ice to EPA Region VIII Laboratory for analysis.
- d. Duplicate 1L amber glass bottles will be collected for diesel range organic (DRO) analysis. These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.
- e. Duplicate 40 mL amber VOA vials will be collected without headspace for gasoline range organic analysis (GRO). These samples will be preserved with HCl, pH <2, and shipped on ice to EPA Region VIII Laboratory for analysis.
- f. Duplicate 40 mL amber VOA vials will be collected for glycol analysis. These samples will be stored and shipped on ice to EPA Region III Laboratory for analysis.
- g. Duplicate 40 mL glass VOA vials will be collected for low molecular weight acids using RSKSOP-112v6. Tribasic Sodium Phosphate (TSP) will be added to the VOA vial prior to shipping to the field for sampling as a preservative. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for GC-MS analysis.
- h. A 1-liter plastic beaker or glass jar will be filled for selected analyses to be conducted in the field. Field measurements will consist of turbidity, alkalinity, ferrous iron, and dissolved sulfide (Table 7). Turbidity (Standard Method 180.1) will be measured using a HACH 2100Q portable turbidimeter (or equivalent instrument). Alkalinity will be measured by titrating ground water with 1.6N H₂SO₄ to the bromcresol green-methyl red endpoint using a HACH titrator (HACH method 8203, equivalent to Standard Method 2320B for alkalinity). Ferrous iron will be measured using the 1,10-phenanthroline colorimetric method (HACH DR/2010 spectrometer, HACH

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method 8146, equivalent to Standard Method 3500-Fe B for wastewater). Dissolved sulfide will be measured using the methylene blue colorimetric method (HACH DR/2010 spectrometer; HACH method 8131, equivalent to Standard Method 4500-S²⁻ D for wastewater).

- 6) After the unfiltered samples have been collected a high-capacity ground-water filter (0.45µm, Pall Corporation, or equivalent manufacturer) will be placed on the end of the pump tubing and filtered samples will be collected into pre-labeled sample bottles. First, approximately 100 mL of ground water will be filtered and sent to waste and next the following series of samples will be collected:
 - a. 125 mL plastic bottle for metals analysis by ICP-OES for Al, Ag, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn, Si, and S; this sample will also be used for ICP-MS analysis for Cd, Cr, As, Cu, Pb, Ni, Se, Hg, and Tl. This sample will be filtered and preserved by adding 5 drops of concentrated HNO₃ (pH test strips will be used to confirm that the sample pH is <2). Test strips for pH will be used on every sample to insure that a proper preservation pH is attained. This is especially important in case high alkalinity samples are encountered during the ground-water sampling. The samples will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.
 - b. One 60 mL clear plastic bottle for CE (capillary electrophoresis) sulfate, chloride, bromide and fluoride. This sample will be filtered, no preservative added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.
 - c. One 60 mL clear plastic bottle for nitrate + nitrite and ammonium. This sample will be filtered, 2 drops of sulfuric acid added as preservative (pH test strips will be used to confirm that the sample pH is <2; see note above regarding use of pH test strips). The samples will be stored and shipped on ice to the RSKERC general parameters lab.
 - d. Duplicate 40 mL glass VOA vial in duplicate for analysis of dissolved inorganic carbon (DIC). This sample will be filtered, no preservative added. The samples will be stored and shipped on ice to the RSKERC general parameters lab.
 - e. Duplicate 40 mL glass VOA vial in duplicate for analysis of dissolved organic carbon (DOC). This sample will be filtered, phosphoric acid added to pH<2. The samples will be stored and shipped on ice to the RSKERC general parameters lab.
 - f. A 20 mL glass VOA will be collected for analysis of δ¹⁸O and δ²H of water using isotope ratio mass spectroscopy (IRMS). The sample will be stored and shipped on ice to Shaw, NRMRL-Ada's on-site contractor for analysis.

- g. A 500 mL clear plastic bottle will be filled for Sr isotope analysis using thermal ionization mass spectroscopy (no acid preservation). The sample will be stored and shipped on ice to the USGS laboratory in Denver, CO.
- h. A 1 L amber plastic bottle will be filled with no preservative added. This sample is an archive sample and will be shipped back to GWERD and stored in a freezer. The archive sample may be used by other parts of the HF study team to support the larger hydraulic fracturing investigation. As an example, analytical methods are being developed by the National Exposure Research Laboratory (NERL). These archived samples could be useful as test samples as those method development studies proceed. Use of these samples would be elaborated in future QAPP revisions.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.2 Domestic wells

The domestic wells and municipal supply wells have a dedicated pump and taps for sampling water from these wells is available (Figure 6). It should be noted that in all cases the samples will be obtained at a point upstream of any water treatment (e.g. water softeners, etc.) which could alter water chemistry. At this time it is unknown to EPA well diameters, well depths, screen intervals, or pump flow rates. However, the QAPP will be updated when this information becomes available.

1. The tap will be turned on. The pump flow rate will be measured to determine if the flow will need to be adjusted. The flow will be regulated to $< 2 \text{ L min}^{-1}$ and a sample will be taken for the monitoring of field parameters. The rate of pumping will be determined by measuring the water volume collected after approximately 15 seconds into a 4 L graduated cylinder; the desirable pumping rate through the flow cell should be less than 2 L min^{-1} and rest of the total flow will be pass through to waste. It is likely that the total flow will not be adjustable and will be measured as described previously. The pumping rate will ideally maintain minimal drawdown, but this may not be possible for these wells since they are designed for purposes other than sampling.
2. The well will be purged for 20 minutes prior to sample collection. After 20 minutes water will be collected for field parameter measurements and a series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.3 Water supply wells

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Water supply wells are designed for high flows to fill water trucks and the flow rates cannot be adjusted and there is no tap in which samples can be collected. Terracon has designed an insert with a tap that is placed between the well and the truck tank to collect samples from (Figure 7).

1. The sampling insert will be connected to the well and to the tanker.
2. The dedicated pump will be powered on. The total flow will not be adjustable and cannot be measured. The pumping rate is likely to cause drawdown, since they are designed for purposes other than sampling.
3. The water will be allowed to flow for one to two minutes to purge the lines of water that is present and the sample collection will be initiated.
4. A series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.2.1.4 North Dakota Water Commission Wells

A portable bladder pumps (QED Sample Pro or equivalent) will be used to sample the one water commission well. The following methodology will be used for the water commission wells.

- 1) Water level measurements will be taken prior to pumping wells. The water level measurements will follow the RSKSOP-326 standard operating procedure. Water levels will be recorded in the field notebook prior to sampling.
- 2) The portable bladder pump will be lowered into the well and the pump intake location will be placed within the screened interval of the well. The tubing connected to the sampling port will be connected to the YSI flow cell. The pump will be powered on. It is expected that the pump will yield a maximum initial flow rate of approximately 50 mL min⁻¹. This flow will pass through a flow cell equipped with an YSI 5600 multiparameter probe (or equivalent probes). The rate of pumping will be determined by measuring the water volume collected after 500 mL of water has been pumped into a 4 L graduated cylinder and the time it takes will be recorded. The pumping rate will ideally maintain minimal drawdown. Water levels will be taken following sampling to confirm the drawdown caused by pumping.
- 3) The YSI probe (or equivalent probes and electrodes) will be used to track the stabilization of pH, oxidation-reduction potential (ORP), specific conductance (SC), dissolved oxygen (DO), and temperature. In general, the guidelines in Table 6 will be used to determine

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when parameters have stabilized. These criteria are initial guidelines; professional judgment in the field will be used to determine on a well-by-well basis when stabilization occurs.

- 4) Once stabilization occurs, the final values for pH, ORP, specific conductance, dissolved oxygen, and temperature will be recorded.
- 5) After the values for pH, ORP, SC, DO, and temperature have been recorded, the flow cell will be disconnected. A series of unfiltered samples and filtered samples will be collected as in section 2.2.1.1 number 5.

See Tables 8 and 9 for numbers of sample bottles needed for each sample type and field QC samples for ground and surface water sampling.

2.3 Sample Handling and Custody

2.3.1 Water Sample Labeling

Each well will be uniquely labeled. Samples collected from each well will include the unique label (Killdeer), well # or name of sample location, the date, the initials of the sampler, and designation of the sample type, e.g., "metals" and preservation technique (when applicable). This information will be recorded onto labeling tape, using water-insoluble ink, affixed to each sample bottle.

2.3.2 Water Sample Packing, Shipping, and Receipt at Laboratories

Samples collected from each location will be placed together in a sealed Ziploc plastic bag. The bags will be placed on ice in coolers. Glass bottles will be packed with bubble wrap to prevent breakage. The coolers will be sent via Fedex, overnight, to the appropriate lab with chain of custody forms (see Figure 9) and custody seal.

R.S. Kerr Environmental Research Center
919 Kerr Research Drive
Ada, OK 74820
580-436-8568 or 580-436-8507
ATTN: Kasie Bennett or Trina Perry
(for samples analyzed by both Shaw and EPA General Parameters Laboratory)

Upon receipt at RSKERC, all samples shall be logged-in and distributed to appropriate analysts by Shaw using RSKSOP-216v2, *Sample Receipt and Log-in Procedures for the On-site Analytical Contractor*. Before opening the ice chests the custody seal is checked by the sample custodian to verify it is intact. Ice chests are opened and the temperature blank is located to take the temperature and it is noted whether or not ice is still present. Chain-of-custody (COC) form

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and samples are removed. Samples are checked against the COC. The observations concerning temperature, custody seal, if ice was not present, and any sample discrepancies are noted on the COC and the sample custodian signs the form. A copy of the COC is distributed to the PI and Shaw retains a copy. The PI should be notified immediately if samples arrive with no ice and/or if the temperature recorded from the temperature blank is greater than or equal to 12° C. These samples will be flagged accordingly.

EPA Region 8 Lab
16194 West 45th Drive
Golden, CO 80403
303-312-7767
ATTN: Jesse Kiernan

Sample receipt and log-in at the Region 8 laboratory shall be conducted as described in their SOP, *Sample Receipt and Control Procedure*, #GENLP-808 Rev. 1.0 and the Region 8 Quality Manual, # QSP-001 Rev. 1.0

US Environmental Protection Agency - Region 3, OASQA
701 Mapes Rd.
Fort Meade, MD 20755-5350
410-305-3032
ATTN: Kevin Martin

Sample receipt and log-in at the Region 3 laboratory shall be conducted as described in their SOP, *Sample Scheduling, Receipt, Log-In, Chain of Custody, and Disposal Procedures*, R3-QA061.

Samples for Sr isotope analysis will be sent to:

Zell Peterman
U.S. Geological Survey
6th and Kipling Sts.
MS 963 Box 25046 DFC
Denver, CO 80225
1-303-236-7883

When the samples are received, the samples are inventoried and checked against the chain-of-custody forms. The date of receipt is indicated on the forms and returned to Doug Beak. The samples are assigned a laboratory number and a cross list is prepared that correlates the assigned number with the field number. The samples are then transferred to their secured chemical laboratory for analysis.

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2.4 Analytical Methods

2.4.1 Ground Water

Ground-water samples will be collected and analyzed using RSKERC standard operating procedures (RSKSOPs) at RSKERC and EPA Methods at the Region VIII laboratory (Table 8).

Region III's LC-MS-MS method for glycols is under development with the intent to eventually have a validated, documented method. The samples are analyzed according to Region III's OASQA (Office of Analytical Services and Quality Assurance) "On Demand" Procedures. See the Region III Laboratory QA Manual, Section 13.1.4.2, *Procedure for Demonstration of Capability for "On-Demand" Data* (Metzger et al., 2011). Aqueous samples are injected directly on the HPLC after tuning MS/MS with authentic standards (2-butoxyethanol, di-, tri-, and tetraethylene glycols) and development of the HPLC gradient. HPLC column is Waters (Milford MA) Atlantis dC18 3 μ m, 2.1 x 150mm column (p/n 186001299). HPLC gradient is with H₂O and CH₃CN with 0.1% formic acid. The 3 glycols are run on a separate gradient than the 2-butoxyethanol. All details of instrument conditions will be included in case file. EPA SW-846 Method 8000B and C are used for basic chromatographic procedures. A suitable surrogate has not been identified. Since there is no extraction or concentration step in sample preparation, extraction efficiency calculations using a surrogate are not applicable. If a suitable surrogate is found, it will be used to evaluate matrix effects. Custom standard mix from Ultra Scientific, (Kingstown RI) is used for the instrument calibration (IC). The working, linear range varies for each compound but is about 10-100 μ g L⁻¹ and may change with further development. Initial Calibration (IC) is performed before each day's sample set, calibration verification is done at the beginning, after every 10 sample injections, and at the end of a sample set. The correlation coefficient (r^2) of the calibration curve must be ≥ 0.99 . An instrument blank is also run after every 10 sample injections. The performance criteria are provided in Table 10. The system is tuned with individual authentic standards (at 1mg L⁻¹ concentration) of each compound according to the manufacturer's directions using the Waters Empower "Intellistart" tune/method development program in the MRM (multiple reaction monitoring) ESI+ (electrospray positive) mode. Tune data is included in the case file. Target masses, transition data and voltages determined in each tune for each compound are compiled into one instrument method. Only one MS tune file (which determines gas flow rates and source temperatures) may be used during a sample set. For these samples, the tetraethylene glycol tune is used as it provides adequate response for all targets. Due to differences in optimal chromatographic separation, the three glycols are analyzed in one run and 2-butoxyethanol is analyzed separately. Exact mass calibration of the instrument is done annually with the preventive maintenance procedure. Mass calibration was successfully performed according to manufacturer's specifications with NaCSl on 6/17/2010 by a certified Waters Corp Service technician. Custom mix supplied by Accustandard (New Haven, CT) is used as a second source verification (SSV). The SSV is run after IC. Matrix spikes and matrix spike duplicates are also performed.

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Analysis at RSKERC includes inductively coupled plasma – optical emission spectroscopy (ICP-OES; for cations), inductively coupled plasma – mass spectroscopy (ICP-MS; for trace metals), capillary electrophoresis (CE, for anions), flow injection analysis (FIA) for N-series), carbon analysis using combustion and infrared detection, gas chromatography (GC, for dissolved gas analysis), isotope ratio mass spectrometry (for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water) and gas chromatography-mass spectroscopy (GC-MS) for VOCs. Analysis by the EPA Region VIII laboratory includes GC for GRO, DRO, and GC-MS for semivolatiles with appropriate sample preparation and introduction techniques. These analytical methods are presented in Table 8.

The RSKSOPs and their associated target analyte list are presented in Table 11. For these analyses, the only surrogates used are for the VOC analysis. Surrogate compounds used are p-bromofluorobenzene and 1,2-dichlorobenzene-d4, spiked at 100 ug/L.

For the semivolatiles the target analyte list is presented in Table 12. Surrogates used include phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14. The concentrations used for the surrogates shall be spiked at $5\text{ }\mu\text{g mL}^{-1}$. For samples containing components not associated with the calibration standards, non-target peaks will be reported as tentatively identified compounds (TICs) based on a library search. Only after visual comparison of sample spectra with the nearest library search results will tentative identifications be made. Guidelines for making tentative identification are:

- A peak must have an area at least 10% as large as the area of the nearest internal standard.
- Major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50 % in the reference spectrum, the corresponding sample ion abundance must be between 30 and 70 %.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Commercial standards for DRO calibration is locally procured DF #2 (source: Texaco station).. Surrogates used in DRO include o-terphenyl at spiking concentrations of $10\text{ }\mu\text{g L}^{-1}$.

Commercial standards for GRO calibration are BTEX, MTBE, naphthalene, and gasoline range hydrocarbons (purchased as certified solutions) and unleaded gasoline from Supelco (product

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number 47516-U). Surrogates used in GRO include 4- bromofluorobenzene at spiking concentrations of $50 \mu\text{g L}^{-1}$.

Strontium isotope ratios will be determined at the USGS laboratory using thermal ionization mass spectrometry (TIMS). A description of the method is provided in Appendix A (Isotope Support for the EPA Hydraulic Fracturing Study by the U.S. Geological Survey (USGS) Denver, CO).

2.5 Quality Control

2.5.1 Quality Metrics for Aqueous Analysis

For analyses done at RSKERC, QA/QC practices (e.g., blanks, calibration checks, duplicates, second source standards, matrix spikes, and surrogates) are described in various in-house Standard Operating Procedures (RSKSOPs) and summarized in Table 13. Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results. Corrective actions are outlined in the appropriate SOPs and when corrective actions occur in laboratory analysis it will be documented and the PI will be notified as to the nature of the corrective action and the steps taken to correct the problem. The PI will review this information and judge if the corrective action was appropriate.

For analyses done by the Region VIII laboratory, QA/QC requirements are:

- (1) Samples shall be processed and analyzed within the following holding times (from date sampled):

Semivolatiles: 7 days until extraction, 30 days after extraction

DRO: 14 days until extraction*, 40 days after extraction

GRO: 14 days*

*With acid preservation

- (2) Data verification shall be performed by the Region VIII laboratory to ensure data meets their SOP requirements.

- (3) Complete data package shall be provided electronically on disk, including copies of chain-of-custody forms, copy of method or Standard Operating Procedure used, calibration data, raw data (including notebook pages), QC data, data qualifiers, quantitation (reporting) and detection limits, deviations from method, and interpretation of impact on data from deviations

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from QC or method requirements. (All documentation needed to be able to re-construct analysis.)

(4) Detection limits (DL) and quantitation (reporting) limits (RL) for the semivolatiles are as provided in Table 12. The DL and RL for DRO and GRO are both at 20 µg/L.

(5) The laboratory shall be subject to an on-site QA audit and analysis of Performance Evaluation samples. If the laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples, a request will be made for this data. If they are not actively involved in analyzing these samples, then they shall be provided by RSKERC.

(6) See Table 14 for QC types and performance criteria.

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by the Region III laboratory, QA/QC requirements are:

- (1) Samples shall be analyzed within the holding time of 14 days.
- (2) Data verification shall be performed by the Region III laboratory to ensure data meets the method requirements.
- (3) Complete data package shall be provided electronically on disk, including copies of chain-of-custody forms, copy of method or Standard Operating Procedure used, calibration data, raw data (including notebook pages), QC data, data qualifiers, quantitation (reporting) and detection limits, deviations from method, and interpretation of impact on data from deviations from QC or method requirements. (All documentation needed to be able to re-construct analysis.)
- (4) Detection and reporting limits are still being determined, but most will be between 10 and 50 ppb (Table 15).
- (5) The laboratory shall be subject to an on-site QA audit if the glycol data becomes "critical" at a later date after method validation.
- (6) See Table 10 for QC types and performance criteria.
- (7) Until the method is validated, the data will be considered "screening" data.

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Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

For analyses done by USGS, QA/QC requirements are (Table 16):

- (1) Data verification shall be performed by USGS to ensure data meets their SOP requirements.
- (2) Complete data packages shall be provided electronically including tabulation of final results, copies of chain-of-custody forms, list of SOPs used (title and SOP #), calibration data, QA/QC data, data qualifiers, deviations from method, and interpretation of impact on data from deviations from QC or method requirements.
- (3) See Table 16 for QC types and performance criteria

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the PI shall be notified. The data will be qualified with a determination as to impact on the sample data. Failures and resulting corrective actions shall be reported.

2.5.2 Measured and Calculated Solute Concentration Data Evaluation

The computer program AqQA (RockWare Inc., version 1.1.1) will be used as a check on the quality of solute concentration data. Two methods will be used. First, the specific conductance values measured in the field will be compared to a calculated value that is based on anion- and cation-specific resistivity constants and the measured concentrations of anions and cations in specific ground-water samples. The agreement between the measured and calculated values should be within 15%. The second method will be to calculate the charge balance for each solution. This is done by summing and comparing the net positive and negative charge from the measured concentrations of anions and cations. The agreement should be within 10%. Poor agreement would suggest that some major solute(s) is not accounted for in the analytical measurements. At the discretion of the PI, discrepancies in this manner will be either flagged or the identity of other sample components and/or reason(s) for poor agreement will be investigated.

2.5.3 Detection Limits

Detection limits for the various analytes are listed in the RSKERC Standard Operating Procedures for these methods and are listed in Table 11. Any updates to these detection limits

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will be provided in their data reports. Detection limits for the analyses done by Region VIII and III are discussed in Section 2.5.1. They are adequate for project objectives. They are adequate for project objectives. For isotope measurements, detection limits do not apply. However, enough mass of the element of interest must be included in the sample. For example, 100 ng of Sr is required to determine the isotope ratio of Sr in a sample. In most cases, mass limitations are not expected for isotope measurements.

2.5.4 QA/QC Calculations

% Recovery or Accuracy

$$\% \text{REC} = \frac{m}{n} \times 100$$

Where m = measurement result

n = True Value (a certified or known value) of standard or reference

Precision

Precision is described by Relative Percent Difference (RPD) as previously defined. The Relative Percent Difference (RPD) is calculated based on the following:

$$\text{RPD} = \frac{2(a-b)}{a+b} \times 100$$

where a = sample measurement and b = duplicate sample measurement and $a > b$.

Matrix Spike Recovery

Matrix spikes sample spiking levels are determined at the discretion of the individual analysts (based on sample concentrations) and are included with the sample results.

$$\% \text{Recovery} = \frac{\text{spiked sample concentration} - \text{native sample concentration}}{\text{spiked sample concentration}} \times 100$$

2.6 Instrument/Equipment Testing, Inspection, and Maintenance

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Laboratory instrumentation used for analysis of project analytes are in routine use and are tested for acceptable performance prior to analyzing actual samples through the analysis of standards and QC samples. Field instruments are tested prior to use in the field by calibrating or checking calibration with standards. Routine inspection and maintenance of these instruments is documented in instrument logbooks. RSKSOPs provide details on instrument testing and corrective actions.

2.7 Instrument/Equipment Calibration and Frequency

RSKERC calibration and calibration frequency are described in RSKSOPs (RSKERC Standard Operating Procedures). For the Region III and Region VIII laboratory, these requirements are identified in their SOPs and in Tables 14 and 10.

Field instruments (meters for pH, specific conductance, ORP, DO, and temperature) are calibrated (per manufacturer's instructions) or checked for calibration daily prior to use, mid-day, and at the end of the day after the last sample measurement. Calibration standards shall be traceable to NIST (Table 6), if available and verified that all dated calibration standards are not beyond their expiration date and will not expire during the field trip. Prior to deployment each test meter will be checked that it is in good working order. Calibration data will be recorded in a bound waterproof notebook and personnel making entries will adhere to the GWERD Notebook policy. Calibration of instruments will be performed daily prior to initiation of sample collection and will be performed according to manufacturer's instructions and will be recorded in the field notebook. In addition calibration checks will be performed using known standards or buffers before use, mid-day and at the end of the day. With the exception of pH all checks must be within $\pm 10\%$ of known concentrations and in the case of pH must be within ± 0.2 pH units. These calibration checks will be recorded in the field notebook. If a calibration check fails, this will be recorded in the field notebook and the possible causes of the failure will be investigated. Upon investigation corrective action will be taken and the instrument will be recalibrated. Samples taken between the last good calibration check and the failed calibration check will be flagged to indicate there was a problem. Duplicate field measurements are not applicable to measurements in flow through cell (RSKSOP-211v3, *Field Analytical QA/QC*).

Hach spectrophotometers (ferrous iron and sulfide) and turbidimeters (turbidity) will be inspected prior to going to the field and their function verified. These instruments are factory-calibrated and will be checked in the lab prior to going to the field per the manufacturer's instructions. For the Hach spectrophotometers this will consist of checking the accuracy and precision for that method. The ferrous iron accuracy will be checked by measuring a $1 \text{ mg Fe}^{2+} \text{ L}^{-1}$ standard and the results should be between $0.90 - 1.10 \text{ mg Fe}^{2+} \text{ L}^{-1}$. Similarly, the precision will be tested using the standard performing the measurement three times on this solution. The single operator standard deviation should be $\pm 0.017 \text{ mg Fe}^{2+} \text{ L}^{-1}$. For sulfide method the precision will be checked using a $0.75 \text{ mg S}^{-} \text{ L}^{-1}$ standard solution and the standard deviation to be obtained is $\pm 0.02 \text{ mg S}^{-} \text{ L}^{-1}$. Turbidity will be checked against turbidity standards supplied by Hach. In addition, blanks (deionized water) will be run at the beginning of the day, midday, and at the end of the day. The values for the blanks will be recorded in the field notebook and

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any problems associated will be recorded. If blanks have detectable concentrations of any analyte the sample cells will be decontaminated and a new blank will be run. This process will continue until there is no detectable analytes in the blanks. Standards for redox sensitive species such as sulfide and ferrous iron are difficult to use in the field because once exposed to atmospheric oxygen their concentrations can change. Similarly calibration standards for alkalinity are sensitive to atmospheric carbon dioxide. Alkalinity measurements will use a 1.6N H_2SO_4 solution to titrate samples and standards in the field. The titrator will be checked using a 250 mg L^{-1} standard made from Na_2CO_3 . The analyzed value should be in the range of 225- 275 mg L^{-1} . Duplicates will be performed once a day or on every tenth sample. Duplicates acceptance criteria are $\text{RPD} \leq 15$. The values obtained for each duplicate sample will be recorded in the field notebook and RPD will be calculated (section 2.5.4) and recorded in the field notebook. If the duplicate samples fail an additional duplicate sample will be taken and reanalyzed. If the additional duplicate samples fail to meet the QC criteria, then the instruments will be checked and corrective action taken. The corrective actions will be recorded in the field notebook. Samples collected between the last valid duplicate sample and the failed duplicate sample will be flagged.

2.8 Inspection/Acceptance of Supplies and Consumables

RSKSOPs and Region VIII SOPs provide requirements for the supplies and consumables needed for each method. The analysts are responsible for verifying that they meet the SOP requirements. Other supplies that are critical to this project are listed in Table 17. It should be noted that the vendors listed in Table 17 are suggested vendor and equivalent parts may be available from other vendors or substitute for based on purchasing rules. Doug Beak is responsible for ensuring these are available and to ensure they are those as listed previously.

2.9 Non-direct Measurements

The locations for the monitoring wells were determined by Terracon Consultants, Inc. the site contractor for Denbury Resources, Inc. Data was made available from the NDIC and NDDWQ. In addition, the USGS published a report on the Killdeer aquifer giving background and characterization information on the Killdeer Aquifer. Since this data will not be reported as a part of this project, but used as background information for this site, the data quality will be considered acceptable if it has met QA/QC requirements of their methods used.

2.10 Data Management

The PI is responsible for maintaining data files, including their security and integrity. All files (both electronic and hard copy) will be labeled such that it is evident that they are for the hydraulic fracturing project at Killdeer, ND.

Data will be submitted to Doug Beak as either hard copies (field notes), or electronically (laboratory data) in Excel spreadsheets on CD or DVD or via email. Data in hard copy form will be manually entered into Excel spreadsheets on Doug Beak's computer or designated GWERD

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staff computer and will given to Doug Beak. Either, Doug Beak or a technician or student will conduct this task. Data will be spot-checked by Doug Beak to ensure accuracy. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found.

Data in electronic form shall be electronically transferred to the spreadsheets. Data will be spot-checked by Doug Beak to ensure accuracy of the transfer. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check of the data set being entered at that time if multiple errors are found.

2.10.1 Data Analysis, Interpretation, and Management

Data validation will consist of initial and final review of data. Initial review will include continuous oversight during field collection of data by the principal investigator to avoid common transcription errors associated with recording of data. Final review will include evaluation of all collected data for suitability in data interpretation. It will include but is not limited to the following activities: (1) assessment of data completeness, (2) review of log books and forms used for data logging, and (3) review of calibration and standard checks.

2.10.2 Data Recording

Data collected during the ground-water investigation will be recorded into field notebooks and entered into EXCEL spreadsheets. Water quality data will also be entered into AqQA a program for evaluating ground water quality and for evaluating data validity. Graphs will be produced using EXCEL or Origin to show key data trends.

2.10.3 Data Storage

As this is a Category I project, all data and records associated with this project will be kept permanently and will not be destroyed. All data generated in this investigation will be stored electronically in Microsoft EXCEL and backed up in RSKERC's local area network 'M' drive. All paper-based records will be kept in the PI's offices. If the project records are archived, Doug Beak will coordinate with GWERD management and GWERD's records liaison and contract support the compiling of all data and records.

2.10.4 Analysis of Data

All data collected associated with groundwater and surface water sampling will be summarized in EXCEL spreadsheets. Data will be spot-checked (10 % of samples) by Doug Beak to ensure accuracy. If errors are detected during the spot-check, the entries will be corrected. Detection of an error will prompt a more extensive inspection of the data, which could lead to a 100% check

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of the data set being entered at that time if multiple errors are found. When possible, data sets will be graphically displayed using EXCEL, Sigma Plot, and Origin to reveal important trends.

3.0 Assessment and Oversight

3.1 Assessments and Response Actions

Technical Systems Audits (TSAs), Audits of Data Quality (ADQs), and Performance Evaluations (if not currently done) will be conducted early in the project to allow for identification and correction of any issues that may affect data quality. TSAs will be conducted on both field and laboratory activities. Laboratory TSAs will focus on the critical target analytes. Detailed checklists, based on the procedures and requirements specified in this QAPP, related SOPs, and EPA Methods will be prepared and used during these TSAs. These audits will be conducted with contract support from Neptune and Co., with oversight by Steve Vandegrift, QAM.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will also be performed by the Neptune and Co., with oversight by Steve Vandegrift, QAM. See Section 4.2 for additional discussion on ADQs.

Performance Evaluations (PE) will be conducted on critical target analytes for those that are available commercially.

See Section 3.2 for how and to whom assessment results are reported.

Assessors do not have stop work authority; however, they can advise the PI if a stop work order is needed in situations where data quality may be significantly impacted, or for safety reasons. The PI makes the final determination as to whether or not to issue a stop work order.

For assessments that identify deficiencies requiring corrective action, the audited party must provide a written response to each finding and observation to the PI and QA Manager, which shall include a plan for corrective action and a schedule. The PI is responsible for ensuring that audit findings are resolved. The QA Manager will review the written response to determine their appropriateness. If the audited party is other than the PI, then the PI shall also review and concur the corrective actions. The QA Manager will track implementation and completion of corrective actions. After all corrective actions have been implemented and confirmed to be completed; the QA Manager shall send documentation to the PI and his supervisor that the audit is closed. Audit reports and responses shall be maintained by the PI in the project file and the QA Manager in the QA files, including QLOG.

3.1.1 Assessments

TSAs will be conducted on both field and laboratory activities. Detailed checklists, based on the procedures and requirements specified in this QAPP, SOPs, and EPA Methods will be prepared and used during these TSAs. One field TSA will be done. It is anticipated this will take place during the first sampling event in July 2011. The laboratory audit will take place when samples are in the laboratory's possession and in process of being analyzed.

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Laboratory TSAs will focus on the critical target analytes (Table 3) and will be conducted on-site at RSKERC (involves both EPA and Shaw-operated labs) and at the Region VIII laboratory which will analyze for semi-volatile organic, DRO and GRO analyses. It is anticipated this will take place immediately following the first sampling event in July.

ADQs will be conducted on a representative sample of data for the critical target analytes. These will begin with the first data packages to ensure there are no issues with the data and to allow for appropriate corrective actions on subsequent data sets if needed.

Performance Evaluations will be conducted on critical target analytes for those that are available commercially. Shaw and the EPA GP Lab analyzes PE samples routinely on a quarterly basis. The Region VIII laboratory is currently analyzing Performance Evaluation (aka Proficiency Testing) samples twice a year and data from the past two studies have been provided to the QAM. Glycols analyzed by Region III are not critical, but even if they become critical, PE samples are not available commercially, so PEs will not be done by their laboratory for glycols.

3.1.2 Assessment Results

At the conclusion of a TSA, a debriefing shall be held between the auditor and the PI or audited party to discuss the assessment results. Assessment results will be documented in reports to the PI, the PI's first-line manager, and the Technical Research Lead for Case Studies. If any serious problems are identified that require immediate action, the QAM will verbally convey these problems at the time of the audit to the PI.

The PI is responsible for responding to the reports as well ensuring that corrective actions are implemented in a timely manner to ensure that quality impacts to project results are minimal.

3.2 Reports to Management

All final audit reports shall be sent to the Technical Research Lead for Case Studies, first-line manager of Doug Beak and copied to Doug Beak. Audit reports will be prepared by the QA Manager or the QA support contractor, Neptune and Co. Those prepared by Neptune and Co. will be reviewed and approved by the QAM prior to release. Specific actions will be identified in the reports.

4.0 Data Validation and Usability

4.1 Data Review, Verification, and Validation

Criteria that will be used to accept, reject, or qualify data will include specifications presented in this QAPP, including the methods used and the measurement performance criteria presented in Tables 9, 10, 13, 14, and 16. In addition, sample preservation and holding times will be evaluated against requirements Table 8.

Data will not be released outside of RSKERC until all study data have been reviewed, verified and validated as described below. The PI is responsible for deciding when project data can be shared with interested stakeholders in conjunction with the GWERDs Director's approval.

4.2 Verification and Validation Methods

Data verification will evaluate data at the data set level for completeness, correctness, and conformance with the method. Data verification will be done by those generating the data. This will begin with the analysts in the laboratory and the personnel in the field conducting field measurements, monitoring the results in real-time or near real-time. At RSKERC, Shaw's, verification includes team leaders, the QC coordinator, and the program manager. For the EPA GP Lab at RSKERC, data verification includes peer analysts in the GP lab and the team leader. Shaw's and the EPA GP Lab's process goes beyond the verification level, as they also evaluate the data at the analyte and sample level by evaluating the results of the QC checks against the RSKSOP performance criteria.

For the Region VIII laboratory, QA/QC requirements include data verification prior to reporting and detailed description can be found in the QSP-001-10 QA Manual (Burkhardt and Batschelet, 2010). Results are reported to the client electronically, unless requested otherwise. Electronic test results reported to the client include the following: Data release memo from the analysts, LQAO, Laboratory Director (or their Designees) authorizing release of the data from the Laboratory, and a case narrative prepared by the analysts summarizing the samples received, test methods, QC notes with identification of noncompliance issues and their impact on data quality, and an explanation of any data qualifiers applied to the data.

The Region III laboratory data verification and validation procedure is described in detail in their Laboratory Quality Manual (Metzger et al., 2011). Briefly, the procedure is as follows. The actual numeric results of all quality control procedures performed must be included in the case file. The data report and narrative must describe any limitations of the data based on a comprehensive review of all quality control data produced. A written procedure or reference must be available for the method being performed and referenced in the narrative. If the method to be performed is unique, the procedures must be fully documented and a copy included in the case file. Verify that the calibration and instrument performance was checked by analyzing a second source standard (SCV). (The concentration of the second source standard must be in the range of the calibration.) Results must be within the method, procedure, client or in-house

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limits. At least one blank (BLK), duplicate analysis, and spiked sample must be carried through the entire method or procedure. Peer reviewers complete the On-Demand Data Checklist. The data report must document the accuracy and precision of the reported data by applying qualifier codes, if applicable, and include a summary of the quality control in the case file.

For field measurements, Doug Beak will verify the field data collected.

The laboratories shall contact the PI upon detection of any data quality issues which significantly affect sample data. They shall also report any issues identified in the data report, corrective actions, and their determination of impact on data quality.

Data validation is an analyte- and sample-specific process that evaluates the data against the project specifications as presented in the QAPP. Data validation will be performed by a party independent of the data collection activity. Neptune and Company, a QA support contractor, will conduct data validation on a representative sample of the critical analytes with oversight by the QAM. Data packages for the critical analytes that have been accepted by Doug Beak as ready to use or report shall be provided to Steve Vandegrift, QAM, who will coordinate the data validation with Neptune. Neptune shall evaluate data against the QAPP specifications. Neptune will use NRMRL SOP #LSAS-QA-02-0, "Performing Audits of Data Quality" as a guide for conducting the data validation. The outputs from this process will include the validated data and the data validation report. The report will include a summary of any identified deficiencies and a discussion on each individual deficiency and any effect on data quality and recommended corrective action.

As part of the data validation process, the synthesis of data and conclusions drawn from the data will be reviewed by the RSKERC Case Study Team (minimally will include case study PIs, Technical Research Lead for case studies, and GWERD Director) prior to release of this information or data to entities outside of RSKERC. Once reviewed by the RSKERC Case Study Team in coordination with the GWERD Director, the GWERD Director will approve its release.

4.3 Reconciliation with User Requirements

The PI, Doug Beak, shall analyze the data, as presented below. Doug Beak shall also review the results from the data verification and validation process. Doug Beak shall make a determination as to whether or not the data quality has met project requirements and thereby the user requirements. If there are data quality issues that impact their use, the impact will be evaluated by the PI. If corrective actions are available that would correct the issue, Doug Beak will make the determination to implement such actions. For example, the PI may have the option to re-sample or re-analyze the affected samples. If not, then the PI will document the impact in the final report such that it is transparent to the data users how the conclusions from the project are affected.

The types of statistical analyses that will be performed include summary statistics (mean, median, standard deviation, minimum, maximum, etc.) if applicable. In addition, the data will be

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plotted graphically over time and trends in the data will be analyzed, for example increasing or decreasing concentrations of a particular analyte.

Data will be presented in both graphical and tabular form. Tabular forms of the data will include Excel spreadsheets for raw data and tables containing the processed data. Graphical representations of the data will not only include time series plots as previously described, but also Durov and Piper Diagrams for major anions and cations. In addition, concentrations of data could be plotted on surface maps of the Killdeer site showing well locations and concentrations of analytes and contours may be developed to show "analyte plumes".

5.0 References

American Public Health Association; American Water Works Association; Water Environment Federation. 1998. Method 3500-Fe B. Phenanthroline Method. In: Standard Methods for the Examination of Water and Waste Water, 20th Ed. Editors Clesceri, L.S.; Greenberg, A.E.; and Eaton, A.D. Washington D.C.

American Public Health Association; American Water Works Association; Water Environment Federation. 1998. Method 4500-S²⁻ D. Methylene Blue Method. 2p In: Standard Methods for the Examination of Water and Waste Water, 20th Ed. Editors Clesceri, L.S.; Greenberg, A.E.; and Eaton, A.D. Washington D.C.

Bade, Michael. 2011. Sample Receipt and Control Procedure. SOP No.: GENLP-808 rev 1.0. EPA Region 8 Laboratory.

Burkhardt, Mark; Datschelet, William. 2010. U.S. EPA Region 8 Environmental Laboratory Quality Assurance Manual. SOP No. QSP-001 rev 1.0. EPA Region 8 Laboratory.

Domenico, Patrick A. and Schwartz, Franklin W. 1990. Physical and Chemical Hydrogeology. John Wiley & Sons, Inc. New York.

Kiernan, Jesse. 2010. Determination of BTEX, MTBE, Naphthalene and TPH/GRO using EPA Method 8021B and 8015D Modified. SOP No.: ORGM-506 rev. 1.0. EPA Region 8 Laboratory.

Kiernan, Jesse. 2010. Determination of Diesel Range Organics Using EPA Method 5015D Modified. SOP No. ORGM-508 rev. 1.0. EPA Region 8 Laboratory.

Klausing, Robert L. 1979. Ground-Water Resources of Dunn County, North Dakota. Report prepared by the U.S. Geological survey for the North Dakota Geological Survey, North Dakota State Water Commission and Dunn County Water Management District. Bismarck, North Dakota.

Marti, Vicente. 2011. Determination of Semivolatile Organic Compounds Using Method 8270D. SOP No. ORGM-515 rev. 1.1. EPA Region 8 Laboratory.

Metzger, Cynthia; Caporale, Cynthia; Bilyeu, Jill. 2011. Laboratory Quality Manual, Version 8. U.S. Environmental Protection Agency Region 3, Environmental Science Center Environmental Assessment and Innovation Division, Office of Analytical Services and Quality Assurance.

RSKSOP-112v6. Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC. 22 p.

RSKSOP-152v3. Ground-Water Sampling. 5 p.

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RSKSOP-175v5. Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique. 33 p.

RSKSOP-179v2. Standard Operating Procedure for Total Nitric Acid Extractable Metals from Aqueous Samples by Microwave Digestion. 9 p.

RSKSOP-194v4. Gas Analysis by Micro Gas Chromatograph (Agilent Micro 3000). 13 p.

RSKSOP-211v3. Field Analytical QA/QC. 4 p.

RSKSOP-212v6. Standard Operating Procedure for Quantitative Analysis of Low Molecular Weight Acids in Aqueous Samples by HPLC. 22 p.

RSKSOP-213v4. Standard Operating Procedure for Operation of Perkin Elmer Optima 3300 DV ICP-OES. 22 p.

RSKSOP-214v5. Quality Control Procedures for General Parameters Analyses using the Lachat Flow Injection Analyses (FIA), 10 p.

RSKSOP-216v2. Sample Receipt and Log-In Procedures for the On-Site Analytical Contractor. 5 p.

RSKSOP-257v3. Operation of Thermo Elemental PQ Excell ICP-MS. 16 p.

RSKSOP-275v1. Collection of Water Samples from Monitoring Wells. 10 p.

RSKSOP-276v3. Determination of Major Anions in Aqueous Samples Using Capillary Ion Electrophoresis with Indirect UV Detection and Empower 2 Software. 11 p.

RSKSOP-296v1. Determination of hydrogen and oxygen isotope ratios in water samples using high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS), 8 p.

RSKSOP-299v1. Determination of Volatile Organic Compounds (Fuel Oxygenates, Aromatic and Chlorinated Hydrocarbons) in Water Using Automated Headspace Gas Chromatography/Mass Spectrometry (Agilent 6890/5973 Quadrupole GC/MS System). 25 p.

RSKSOP-326v0. Manual Measurement of Groundwater Levels for Hydrogeologic Characterization. 4 p.

RSKSOP-330v0. Determination of Various Fractions of Carbon in Aqueous Samples Using the Shimadzu TOC-VCPH Analyzer. 15 p.

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RSKSOP-332v0. Standard Operating Procedure for Operation of Thermo X Series II ICP-MS.
16 p.

Shaver, Robert. 2009. Water Availability for Oil Well Development in North Dakota and Status of Water Depot Permit Applications. North Dakota State Water Commission, Water Appropriations Division.

USEPA Method 180.1. Determination of Turbidity by Nephelometry, 10p.

USEPA Method 2320. Carbonate, Bicarbonate, and Total Alkalinity, 3p.

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6.0 Tables

Table 1. Known constituents of the Hydraulic Fracturing Fluid Component use for the Franchuk well.

Active Ingredients	CAS Number	Chemical Formula
Glutaraldehyde	111-30-8	C ₅ H ₈ O ₂
Alkyl dimethyl ethylbenzyl chloride (68% C12, 32% C14)	85409-23-0	
Alkyl dimethyl benzyl ammonium chloride (C12 -18)	68391-01-5	
Tert-Butyl Hydroperoxide	75-91-2	C ₄ H ₁₀ O ₂
Acetic Acid	64-19-7	C ₂ H ₄ O ₂
Potassium Hydroxide	1310-58-3	KOH
Potassium Carbonate	584-08-7	KC ₂ O ₃
Ethoxylated nonyl phenol	9016-45-9	C ₁₇ H ₂₈ O ₂
Sodium Tetraborate	1330-43-4	Na ₂ B ₄ O ₇
Amine Phosphonate 1	Proprietary	
Methanol	67-56-1	CH ₄ O
Hydrochloric Acid	7647-01-0	HCl
Isopropyl Alcohol	67-63-0	C ₃ H ₈ O
2-Ethylhexanol	104-76-7	C ₈ H ₁₈ O
Diethylenetriamine	111-40-0	C ₄ H ₁₂ N ₃
Heavy Aromatic Solvent Naphtha	64742-94-5	
Naphthalene	91-20-3	C ₁₀ H ₈
Benzene, 1-1'-oxybis-, tetrapropylene derivatives, sulfonated	119345-03-8	
Diethylenetriamine Alkylbenzene Sulfate	40139-72-8	
Tetramethylammonium Chloride	75-57-0	C ₄ H ₁₂ ClN
2-Ethylhexanol	104-76-7	C ₈ H ₁₈ O
Acetic acid	64-19-7	C ₂ H ₄ O ₂
Acrylamide	76-06-1	C ₃ H ₅ NO
Acrylamide sodium	38193-60-1	
Alcohols, C10-16, ethoxylated	68002-97-1	
Benzene, 1-1'-oxybis-, tetrapropylene derivatives, sulfonated	119345-03-8	C ₃₆ H ₅₈ O ₇ S ₂
Boric Acid	1303-86-2	B(OH) ₃
Canola Oil		
Colemanite	1318-33-8	CaB ₃ O ₄ (OH) ₃ ·H ₂ O
dihexamethylenetriaminepentakis(methylene phosphonic acid) [aka - amine phosphonate]	119345-03-8	(C ₁₇ H ₄₄ N ₃ O ₁₅ P ₅)
Disodium ethylenediaminetetraacetate	38011-25-5	Na ₂ C ₁₀ H ₁₄ N ₂ O ₈

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Dowicil 75	4080-31-3	$C_9H_{16}Cl_2N_4$
Emulsion Breaker	29316-47-0	
Emulsion Breaker	153795-76-7	
Emulsion Breaker	68036-95-3	
Emulsion Breaker	30704-64-4	
Ethoxylated sorbitan monostearate	9005-67-8	$C_{54}H_{106}O_{21}$
formaldehyde	50-00-0	CH_2O
Hydroxypropyl Guar	39421-75-5	
Mineral Oil	64742-46-7	
Organophilic Clay	68953-58-2	
Petroleum Distillate Blend	64741-84-1	
Phosphoric Acid	7664-38-2	H_3PO_4
Propylene Carbonate	108-32-7	$C_4H_6O_3$
Sodium Chloride	7647-14-5	$NaCl$
Sodium Glycolate	2836-32-0	$NaC_2H_3O_3$
Sodium hydroxide	1310-73-2	$NaOH$
Sorbitan monooleate	1338-43-8	$C_{24}H_{44}O_6$
Tetrasodium ethylenediaminetetraacetate	64-02-8	$Na_4C_{10}H_{12}N_2O_8$
triethanolamine hydrochloride	637-39-8	$C_6H_{15}O_3N HCl$
Trisodium ethylenediaminetetraacetate	19019-43-3	$Na_3C_{10}H_{13}N_2O_8$
Trisodium nitrilotriacetate	5064-31-3	$Na_3C_6H_6NO_6$
Xanthan gum	various CAS #s listed	

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Table 2 . The physical characteristics of the monitoring wells near the Franchuk 44-20SWH well (Data provided by NDIC and Terracon Consultants, Inc.)^{*}.

Monitoring Well	Screen Interval (ft)	Screen Length (ft)	Total Depth (ft)
MW-1	37- 47	10	47
MW-2	37-47	10	47
MW-3	27-42	15	42
MW-4	32-72	40	72
MW-5	30-45 [†]	15 [†]	45 [†]
MW-6	30-45 [†]	15 [†]	45
MW-7	55-70 [†]	15 [†]	70 [†]
MW-8S [‡]	80-120 [†]	60 [†]	120 [†]
MW-8D [‡]	180-245 [†]	65 [†]	245 [†]
██████ [§]			
██████ [§]			
██████ [§]	90-110	20	110
Pavlenko Depot North ^{***}	70-140	70	140
Pavlenko Depot South ^{***}	87-167	80	172
Missouri Basin Depot ^{***}	130-170	40	170
Truchan Depot ^{***}	90-175	85	180
CW#4 [§]	140-165	25	165
CW#5 [§]	85-125	40	125

^{*} Only limited information for these well has been supplied to EPA at this time.

[†] Information provided by Terracon to the State of ND in a proposal. The exact depths, screen intervals and lengths need to be verified once the wells are surveyed in the Summer 2011.

[‡] Well cluster.

^{**} Domestic well

^{***} Water Supply well

[§] City of Killdeer municipal well

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Table 3. Critical analytes.

Analyte	Analysis Method	Laboratory Performing the Analysis
Gasoline Range Organics (GRO)	ORGM-506 r1.0, EPA Method 8015D	EPA Region VIII Laboratory
Diesel Range Organics (DRO)	ORGM-508 r1.0, EPA Method 8015D	EPA Region VIII Laboratory
Volatile Organic Compounds (VOC)*	RSKSOP-299v1	Shaw Environmental
Semivolatile Organic Compounds (SVOC)	ORGM-515 r1.1, EPA Method 8270D	EPA Region VIII Laboratory
Dissolved Gases**	RSKSOP-194v4 & -175v5	Shaw Environmental
Metals (As, Se, Sr, Ba, B)	RSKSOP-213v4 & -257v2 or -332v0	Shaw Environmental
Major Cations (Ca, Mg, Na, K)	RSKSOP-213v4	Shaw Environmental
Major Anions (Cl, NO ₃ ⁻ +NO ₂ ⁻ , SO ₄ ²⁻)	RSKSOP-276v3 (RSKSOP-214v5 for NO ₃ ⁻ +NO ₂ ⁻)	RSKERC general parameters lab

*alcohols (isopropyl alcohol and t-butyl alcohol), naphthalene (using RSKSOP-299v1)

**methane, ethane, propane, butane

Only those SVOC compounds in Table 12 that have DL, RL, and Control Limits listed may be used as critical analytes. Others only as screening data.

Both VOC and SVOC have many target analytes and initially all are considered as critical (with exception for SVOC noted above). A tiered approach will be used to further refine the identification of specific compounds as critical. Data from the first sampling events will be evaluated by the PI to determine if there are specific compounds that are identified in these samples which would warrant their specific identification as critical to narrow the list. These will be identified in a subsequent QAPP revision.

GRO analysis provides data for not only TPH as gasoline, but several other compounds. Only TPH as gasoline will be considered critical from this analysis.

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Table 4. Tentative schedule of field activities for the Hydraulic Fracturing Case Study Bakken Shale, Killdeer and Dunn County, ND.

Media	July 2011	October 2011	November 2011	January 2012	April 2012	August 2012
Groundwater	XXX	XXX	XXX	XXX	XXX	XXX

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Table 5. Water quality of the Killdeer Aquifer. Data from Klausing, 1979.

Parameter	Minimum	Maximum	Mean
TDS (mg L ⁻¹)	234	5030	1531
Na (mg L ⁻¹)	50	1350	413
HCO ₃ ⁻ (mg L ⁻¹)	374	1250	713
SO ₄ ²⁻ (mg L ⁻¹)	33	3000	626
Cl ⁻ (mg L ⁻¹)	0	25	4.5
F ⁻ (mg L ⁻¹)	0.1	1.6	0.66
Fe (µg L ⁻¹)	0	5500	1029
NO ₃ ⁻ (mg L ⁻¹)	0.3	6.7	1.2
B (µg L ⁻¹)	0	3700	534

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Table 6. Field parameter stabilization criteria and calibration standards.

Parameter	Stabilization Criteria	Calibration Standards
pH	$\leq 0.02 \text{ pH units min}^{-1}$	pH 4, 7, and 10 buffers
Oxidation Reduction Potential (ORP)	$\leq 2 \text{ mV min}^{-1}$	Zobells Solution
Specific Conductance (SC)	$\leq 1\% \text{ min}^{-1}$	1413 μS Conductivity Standard

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Table 7. Ground Water Field Analytical Methods.

Parameter	Method	Equipment
Alkalinity	Standard Method 2320B; HACH method 8203	HACH Model AL-DT Digital Titrator (or equivalent device)
Ferrous Fe	Standard Method 3500-Fe B; HACH Method 8146	HACH DR890 Portable Colorimeter (or equivalent device)
Dissolved Sulfide	Standard Method 4500-S ²⁻ D; HACH Method 8131	HACH DR890 Portable Colorimeter (or equivalent device)
Turbidity	EPA Method 180.1	HACH 2100Q Portable Turbidimeter

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Table 8. Ground and Surface Water Sample Collection.

Sample Type	Analysis Method (EPA Method)	Sample Bottles/# of bottles*	Preservation/ Storage	Holding Time(s)
Dissolved gases	RSKSOP-194v4 &-175v5 (No EPA Method)	60 mL serum bottles/2	No Headspace TSP ⁺ , pH>10; refrigerate ≤6°C ^{††}	14 days
Metals	RSKSOP-213v4 &-257v2 or -332v0 (EPA Methods 200.7 and 6020)	125 mL plastic bottle/1	HNO ₃ , pH<2	6 months (Hg 28 days)
SO ₄ , Cl, F, Br	RSKSOP-276v3 (EPA Method 6500)	60 mL plastic/1	Refrigerate≤6°C	28 days
NO ₃ + NO ₂ , NH ₄	RSKSOP-214v5 (EPA Method 350.1)	60 mL plastic/1	H ₂ SO ₄ , pH<2; refrigerate ≤6°C	28 days
DIC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	refrigerate ≤6°C	14 days
DOC	RSKSOP-330v0 (EPA Method 9060A)	40 mL clear glass VOA vial/2	2- H ₃ PO ₄ , pH<2; refrigerate ≤6°C	28 days
Volatile organic compounds (VOC)	RSKSOP-299v1 (EPA Method 5021A+8260C)	40 mL amber glass VOA vial/2	No Headspace TSP ⁺ , pH>10; refrigerate ≤6°C	14 days
Low Molecular Weight Acids	RSKSOP-112v6 (No EPA Method)	40 mL glass VOA vial/2	TSP ⁺ , pH>10; refrigerate≤6°C	30 days
O, H stable isotopes of water	RSKSOP-296v0 (No EPA Method)	20 mL glass VOA vial/1?	Refrigerate at ≤6°C	stable
Semi-volatile organic compounds	ORGM-515 r1.1, (EPA Method 8270D)	1L Amber glass bottle/2 and for every 10 samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample	Refrigerate ≤6°C	7 days until extraction, 30 days after extraction
DRO	ORGM-508 r1.0, (EPA Method	1L Amber glass bottle/2 and for every 10	HCl, pH<2; refrigerate ≤6°C	7 days until extraction,

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	8015D)	samples of ground water need 2 more bottles for one selected sample, or if <10 samples collected, collect 2 more bottles for one select sample		40 days after extraction
GRO	ORGM-506 r1.0, (EPA Method 8015D)	40 mL amber glass VOA vial/2	No Headspace HCl, pH<2; refrigerate $\leq 6^{\circ}\text{C}$	14 days
Gylcols	Region III method** (No EPA Method)	40 mL amber glass VOA vial/2	Refrigerate $\leq 6^{\circ}\text{C}$	14 days
$^{87}\text{Sr}/^{86}\text{Sr}$ analysis	Thermal ionization mass spectrometry (No EPA Method)	500 mL plastic bottle/2	Refrigerate $\leq 6^{\circ}\text{C}$	No information
Archive	NA	1 L plastic amber	Freeze $\leq -10^{\circ}\text{C}$; freezer at lab	NA

[†] trisodium phosphate

^{††} above freezing point of water

*Spare bottles made available for laboratory QC samples and for replacement of compromised samples (broken bottle, QC failures, etc.).

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Table 9. Field QC Samples for Water Samples

QC Sample	Purpose	Method	Frequency	Acceptance Criteria/Corrective Action
Trip Blanks (VOCs and Dissolved Gases only)	Assess contamination during transportation.	Fill bottles with reagent water and preserve, take to field and returned without opening.	One in each ice chest with VOA and dissolved gas samples.	<RL*; if >RL, PI will determine if significant relative to sample data.
Equipment Blanks (Metals, SO ₄ , Cl, F, Br, NO ₃ + NO ₂ , NH ₄ , DOC, DIC, and ⁸⁷ Sr/ ⁸⁶ Sr analysis)	Assess contamination from field equipment, sampling procedures, decon procedures, sample container, preservative, and shipping.	Apply only to samples collected via equipment, such as filtered samples: Reagent water is filtered and collected into bottles and preserved same as filtered samples.	One per day of sampling	<RL; if >RL, PI will determine if significant relative to sample data.
Field Duplicates (All analytes)	Represent precision of field sampling, analysis, and site heterogeneity.	One or more samples collected immediately after original sample.	One in every 10 samples, or if <10 samples collected for a water type (ground or surface), collect a duplicate for one sample**	Report duplicate data; if RPD > 30 for results greater than 5xRL, the affected data will be flagged as needed.
Temperature Blanks	Measure temperature of samples in the cooler.	Water sample that is transported in cooler to lab.	One per cooler.	Record temperature; condition noted on COC form***
Field Blanks (All analytes except isotopes)	Assess contamination introduced from sample container with applicable preservative.	In the field, reagent water is collected into sample containers with preservatives.	One per day of sampling	<RL; if >RL, PI will determine if significant relative to sample data.

*Reporting Limit or Quantitation Limit

**At least two per sampling event if >12 samples are collected.

*** The PI should be notified immediately if samples arrive with no ice and/or if the temperature recorded from the temperature blank is greater than or equal to 12° C. These samples will be flagged accordingly.

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Table 10. Region III Laboratory QA/QC Requirements for Glycols.

QC Type	Performance Criteria	Frequency
Method Blanks	<RL	One per every 20 samples
Solvent Blanks	<RL	One per every 10 samples
Initial and Continuing Calibration Checks	80-120% of expected value	At beginning of sample set, after every tenth sample, and end of sample set
Second Source Standards	80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	80-120% of expected value	One per analytical batch or every 20 samples, whichever is greater
Matrix Spikes (MS)	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	$RPD \leq 25$	One per sample set or every 20 samples, whichever is more frequent

RL = Reporting Limit

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

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Table 11. RSKERC Detection limits for various analytes.

Analyte	Method	MDL ($\mu\text{g L}^{-1}$)	QL or LOQ ($\mu\text{g L}^{-1}$)
VOCs			
Vinyl chloride	RSKSOP-299v1	0.18	0.50
Ethanol	RSKSOP-299v1	18.0	100
1,1-Dichloroethene	RSKSOP-299v1	0.12	0.50
Acetone	RSKSOP-299v1	3.45	10.0
Isopropyl alcohol	RSKSOP-299v1	2.37	10.0
Carbon disulfide	RSKSOP-299v1	0.21	0.50
Methylene chloride	RSKSOP-299v1	0.21	1.00
t-Butyl alcohol	RSKSOP-299v1	2.41	10.0
Methyl t-butyl ether	RSKSOP-299v1	0.09	1.00
t-1,2-Dichloroethene	RSKSOP-299v1	0.10	0.50
1,1-Dichloroethane	RSKSOP-299v1	0.13	0.50
Diisopropyl ether	RSKSOP-299v1	0.11	1.00
Ethyl t-butyl ether	RSKSOP-299v1	0.08	1.00
c-1,2-Dichloroethene	RSKSOP-299v1	0.14	0.50
Chloroform	RSKSOP-299v1	0.13	0.50
1,1,1-Trichloroethane	RSKSOP-299v1	0.13	0.50
Carbon tetrachloride	RSKSOP-299v1	0.12	0.50
Benzene	RSKSOP-299v1	0.06	0.50
1,2-Dichloroethane	RSKSOP-299v1	0.21	0.50
t-Amyl methyl ether	RSKSOP-299v1	0.09	1.00
Trichloroethene	RSKSOP-299v1	0.09	0.50
Toluene	RSKSOP-299v1	0.08	0.50
1,1,2-Trichloroethane	RSKSOP-299v1	0.21	0.50
Tetrachloroethene	RSKSOP-299v1	0.13	0.50
Chlorobenzene	RSKSOP-299v1	0.08	0.50
Ethyl benzene	RSKSOP-299v1	0.06	0.50
m/p-Xylene	RSKSOP-299v1	0.09	1.00
o-Xylene	RSKSOP-299v1	0.08	0.50
Isopropyl benzene	RSKSOP-299v1	0.05	0.50
1,3,5-Trimethylbenzene	RSKSOP-299v1	0.05	0.50
1,2,4-Trimethylbenzene	RSKSOP-299v1	0.05	0.50
1,3-Dichlorobenzene	RSKSOP-299v1	0.16	0.50
1,4-Dichlorobenzene	RSKSOP-299v1	0.17	0.50
1,2,3-Trimethylbenzene	RSKSOP-299v1	0.07	0.50
1,2-Dichlorobenzene	RSKSOP-299v1	0.10	0.50
Naphthalene	RSKSOP-299v1	0.31	1.00
Metals ICP-MS		MDL ($\mu\text{g L}^{-1}$)	QL or LOQ ($\mu\text{g L}^{-1}$)

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As	RSKSOP-257v3/-332v0	0.050/0.052	0.167/0.173
Be	RSKSOP-257v3/-332v0	0.005/0.005	0.015/0.015
Analyte	Method	MDL ($\mu\text{g L}^{-1}$)	QL or LOQ ($\mu\text{g L}^{-1}$)
Cd	RSKSOP-257v3/-332v0	0.020/0.020	0.067/0.067
Cr	RSKSOP-257v3/-332v0	0.037/0.008	0.124/0.027
Cu	RSKSOP-257v3/-332v0	0.287/0.287	0.957/0.957
Fe	RSKSOP-257v3/-332v0	0.105/0.105	0.350/0.350
Hg	RSKSOP-257v3/-332v0	0.019/0.019	0.064/0.064
Mn	RSKSOP-257v3/-332v0	0.037/0.037	0.124/0.124
Mo	RSKSOP-257v3/-332v0	0.008/0.008	0.027/0.027
Ni	RSKSOP-257v3/-332v0	0.048/0.048	0.160/0.160
Pb	RSKSOP-257v3/-332v0	0.043/0.043	0.143/0.143
Sb	RSKSOP-257v3/-332v0	0.014/0.014	0.047/0.047
Se	RSKSOP-257v3/-332v0	0.159/0.044	0.530/0.147
Sr	RSKSOP-257v3/-332v0	0.012/0.012	0.040/0.040
Tl	RSKSOP-257v3/-332v0	0.004/0.004	0.013/0.013
V	RSKSOP-257v3/-332v0	0.003/0.013	0.010/0.044
Zn	RSKSOP-257v3/-332v0	0.072/0.072	0.240/0.240
U	RSKSOP-257v3/-332v0	0.002/0.002	0.007/0.007
Ce	RSKSOP-257v3/-332v0	0.006/0.006	0.020/0.020
Metals ICP-OES		MDL (mg L^{-1})	QL or LOQ (mg L^{-1})
Na	RSKSOP-213v4	0.046	0.154
K	RSKSOP-213v4	0.029	0.097
Ca	RSKSOP-213v4	0.026	0.087
Mg	RSKSOP-213v4	0.013	0.044
Fe	RSKSOP-213v4	0.013	0.044
Mn	RSKSOP-213v4	0.001	0.004
Co	RSKSOP-213v4	0.001	0.004
Mo	RSKSOP-213v4	0.001	0.004
Al	RSKSOP-213v4	0.024	0.080
As	RSKSOP-213v4	0.007	0.024
Se	RSKSOP-213v4	0.007	0.024
Cd	RSKSOP-213v4	0.001	0.004
Be	RSKSOP-213v4	0.001	0.004
Cu	RSKSOP-213v4	0.002	0.007
Sb	RSKSOP-213v4	0.008	0.027
Cr	RSKSOP-213v4	0.001	0.004
Ni	RSKSOP-213v4	0.001	0.004
Zn	RSKSOP-213v4	0.005	0.017
Ag	RSKSOP-213v4	0.003	0.010
Tl	RSKSOP-213v4	0.009	0.030
Pb	RSKSOP-213v4	0.003	0.010

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Sr	RSKSOP-213v4	0.001	0.004
Analyte	Method	MDL (mg L ⁻¹)	QL or LOQ (mg L ⁻¹)
V	RSKSOP-213v4	0.002	0.007
Ba	RSKSOP-213v4	0.001	0.004
B	RSKSOP-213v4	0.005	0.017
Ti	RSKSOP-213v4	0.001	0.004
Si	RSKSOP-213v4	0.019	0.064
P	RSKSOP-213v4	0.011	0.037
S	RSKSOP-213v4	0.026	0.087
U	RSKSOP-213v4	0.009	0.030
Dissolved Gases*		MDL (µg L ⁻¹)	QL or LOQ (µg L ⁻¹)
Methane	RSKSOP-194v4 & RSKSOP-175v5	0.08	1.5
Ethylene	RSKSOP-194v4 & RSKSOP-175v5	0.56	4.11
Ethane	RSKSOP-194v4 & RSKSOP-175v5	0.20	2.91
Acetylene	RSKSOP-194v4 & RSKSOP-175v5	2	18.7
Carbon Dioxide	RSKSOP-194v4 & RSKSOP-175v5	20.4	262
Propane	RSKSOP-194v4 & RSKSOP-175v5	0.24	4.1
Butane	RSKSOP-194v4 & RSKSOP-175v5	0.22	5.22
Hydrogen	RSKSOP-194v4 & RSKSOP-175v5	0.01	0.33
DIC/DOC		MDL (mg L ⁻¹)	QL or LOQ (mg L ⁻¹)
DOC	RSKSOP-330v0	0.067	0.50
DIC	RSKSOP-330v0	0.017	0.50
Anions		MDL (mg L ⁻¹)	QL or LOQ (mg L ⁻¹)
Br ⁻	RSKSOP-276v3	0.248	1.00
Cl ⁻	RSKSOP-276v3	0.118	1.00
SO ₄ ²⁻	RSKSOP-276v3	0.226	1.00
NO ₃ ⁻ + NO ₂ ⁻	RSKSOP-214v5	0.014	0.10
F ⁻	RSKSOP-276v3	0.052	0.20

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NH ₄ ⁺	RSKSOP-214v5	0.012	0.05
Low Molecular Weight Acids	Method	MDL (mg L ⁻¹)	QL (mg L ⁻¹)
Lactate	RSKSOP-112v6	0.020	0.100
Isobutyrate	RSKSOP-112v6	0.018	0.100
Acetate	RSKSOP-112v6	0.011	0.100
Propionate	RSKSOP-112v6	0.022	0.100
Formate	RSKSOP-112v6	0.015	0.100
Butyrate	RSKSOP-112v6	0.025	0.100

*Aqueous concentrations are dependent on headspace volume, aqueous volume, temperature, pressure, etc. These limits were calculated based on a 60 mL bottle, 6 mL headspace, 25 degrees C, headspace pressure of 1 atm, and using the "created" headspace calculations.

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Table 12. Region VIII Detection and Reporting limits and LCS and MS control limits for semivolatile organic compounds (SVOC) using Method 8270.

Analyte	Detection Limits		Control Limits			
	DL ($\mu\text{g L}^{-1}$)	RL ($\mu\text{g L}^{-1}$)	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
1-Chloronaphthalene						
1,2-Dibromo-3-chloropropane						
1,2-Dichlorobenzene	0.218	0.500	67.3	11.4	33	102
1,2-Dinitrobenzene						
1,2-Diphenylhydrazine			84.8	9.4	57	113
1,2,4-Trichlorobenzene	0.208	0.500	71.7	11.6	37	107
1,2,4,5-Tetrachlorobenzene						
1,3-Dichlorobenzene	0.226	0.500	64.8	10.9	32	98
1,3-Dinitrobenzene						
1,4-Dichlorobenzene	0.225	0.500	64.8	10.9	32	98
1,4-Dinitrobenzene						
2-Chloronaphthalene	0.167	0.500				
2-Chlorophenol	0.243	0.500	71.3	11.4	37	106
2-Fluorobiphenyl (Surrogate)			79.9	10.6	48	112
2-Fluorophenol (Surrogate)			63.7	14.8	19	108
2-Methylnaphthalene	0.190	0.500	75.0	9.5	46	104
2-Methylphenol	0.217	0.500	73.3	11.7	38	109
2-Nitroaniline	0.118	0.500	81.8	11.2	48	115
2-Nitrophenol	0.197	0.500	75.8	12.4	39	113
2,3,4,6-Tetrachlorophenol						
2,4-Dichlorophenol	0.185	0.500	76.3	9.6	48	105
2,4-Dimethylphenol	0.142	0.500	68.8	13.5	28	109
2,4-Dinitrophenol	2.00	2.00	75.8	20.6	14	138
2,4-Dinitrotoluene	0.086	0.500	84.3	11.2	51	118
2,4,5-Trichlorophenol	0.151	0.500	79.7	10.3	49	111
2,4,6-Tribromophenol (Surrogate)			82.9	13.6	42	124
2,4,6-Trichlorophenol	0.166	0.500	80.7	10.7	49	113
2,6-Dichlorophenol			82.7	11.3	49	117
2,6-Dinitrotoluene	0.091	0.500				
3-Methylphenol	0.189	0.500	71.3	13	32	110
3-Nitroaniline	0.394	0.500	72.6	17.7	19	126
3,3'-Dichlorobenzidine			65.2	15.3	19	111
4-Bromophenyl phenyl ether	0.108	0.500	82.9	10.2	52	113
4-Chloroaniline	0.546	1.00	62.2	15.6	15	109
4-Chloro-3-methylphenol	0.165	0.500	78.6	10.7	47	111
4-Chlorophenyl phenyl ether	0.120	0.500	80.6	10.3	50	111

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4-Methylphenol	0.189	0.500	71.3	13.0	32	110
4-Nitroaniline	0.320	0.500	77.2	13.7	36	118
4-Nitrophenol	0.085	0.500				
4,4'-DDD						
4,4'-DDE						
4,4'-DDT						
4,4'-Methylenebis (2-chloroaniline)						
4,4'-Methylenebis (N,Ndimethylaniline)						
4,6-Dinitro-2-methylphenol	0.202	0.500	84.9	15.0	40	130
Acenaphthene	0.147	0.500	77.6	10.1	47	108
Acenaphthylene	0.139	0.500	78.5	9.4	40	107
Acetophenone						
Aldrin						
Aniline						
Anthracene	0.088	0.500	83.0	9.7	54	112
Azinphos-methyl						
Azobenzene	0.102	0.500				
Benzoic acid						
Benz(a)anthracene	0.079	0.500	82.7	8.9	56	109
Benzo(b)fluoranthene	0.081	0.500	81.8	12.1	45	118
Benzo(k)fluoranthene	0.088	0.500	84.6	13.2	45	124
Benzo(g,h,i)perylene	0.098	0.500	80.5	14.1	38	123
Benzo(a)pyrene	0.083	0.500	81.3	9.5	53	110
Benzyl alcohol			71.0	13.8	30	112
α-BHC						
β-BHC						
δ-BHC						
γ-BHC (Lindane)						
Bis(2-chloroethoxy)methane	0.183	0.500	76.2	10.2	46	107
Bis(2-chloroethyl) ether	0.238	0.500	73.3	12.3	37	110
Bis(2-chloroisopropyl) ether	0.426	0.500	78.2	17.5	26	131
Bis(2-ethylhexyl) phthalate	0.500	1.00	84.2	14.0	42	126
Butyl benzyl phthalate	0.190	0.500	81.1	11.7	46	116
Carbaryl						
Carbazole	0.084	0.500	82.5	11.4	48	117
Chlorobenzilate						
Chrysene	0.079	0.500	82.1	8.9	55	109
Dibenz(a,h)anthracene	0.110	0.500	84.7	14.1	42	127
Dibenzofuran	0.133	0.500	80.3	8.8	54	107
Di-n-butyl phthalate	0.153	0.500				
Dichlorovos						
Dieldrin						
Diethyl phthalate	0.099	0.500	79.2	12.9	41	118

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Dimethyl phthalate	0.107	0.500	75.9	16.9	25	127
Dinoseb						
Diphenylamine						
Di-n-butyl phthalate			84.8	10.3	54	116
Di-n-octyl phthalate	0.188	0.500	87.4	16.6	37	137
Disulfoton						
Endosulfan I						
Endosulfan II						
Endosulfan sulfate						
Endrin						
Endrin aldehyde						
Endrin ketone						
Fluoranthene	0.094	0.500	85.2	10.4	54	116
Fluorene	0.120	0.500	80.6	10.3	50	112
Heptachlor						
Heptachlor epoxide						
Hexachlorobenzene	0.116	0.500	82.3	10.0	52	112
Hexachlorobutadiene	0.225	0.500	65.2	12.6	27	103
Hexachlorocyclopentadiene	0.202	0.500				
Hexachloroethane	0.196	0.500	60.9	11.1	28	94
Indeno(1,2,3-cd)pyrene	0.093	0.500	84.3	13.6	43	125
Isophorone	0.167	0.500	81.0	10.5	50	112
Malathion						
Methoxychlor						
Mevinphos						
Naphthalene	0.212	0.500	70.8	10.5	39	102
Nitrobenzene	0.233	0.500	76.8	10.8	44	109
Nitrobenzene-d5 (Surrogate)			76.0	11.8	41	111
N-Nitrosodi-n-butylamine	0.187	0.500				
N-Nitrosodiethylamine						
N-Nitrosodimethylamine			67.9	41.1	26	110
N-Nitrosodiphenylamine			79.6	10.6	48	111
N-Nitrosodi-n-propylamine			80.9	15.7	34	128
N-Nitrosomethylethylamine						
Parathion						
Pentachlorobenzene						
Pentachlorophenol	0.199	0.500	77.6	13.3	38	117
Phenanthrene	0.107	0.500	84.0	11.0	51	117
Phenol	0.246	0.500				
Phorate						
Pronamide						
Pyrene	0.087	0.500	88.6	13.2	49	128
Pyridine						
Terbufos						
Terphenyl-d14 (Surrogate)			92.7	14.0	51	135

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Trifluralin					
®-(+)-Limonene	0.054	0.100			
1,3-Dimethyl adamantane	0.028	0.100			
2-Butoxyethanol	0.054	0.100			
Adamantane	0.033	0.100			
Squalene	0.565	1.00			
Terpinol	0.031	0.100			
Tri(2-butoxyethyl)phosphate	0.133	0.200			
GRO	MDL (µg L ⁻¹)	MRL (µg L ⁻¹)			
Benzene	1.0	1.0			
Bromofluorobenzene	0.05	1.0			
Ethyl benzene	1.0	1.0			
m,p-Xylene	2.0	2.0			
Methyl tert-butyl ether	1.0	1.0			
Naphthalene	2.0	2.0			
O-Xylene	1.0	1.0			
Toluene	2.0	2.0			
TPH as gasoline	20.0	20.0			

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Table 13. RSKERC Laboratory QA/QC Requirements Summary* from SOPs.

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Dissolved gases	RSKSOP-194v4 & 175v5*	≤MDL (He blank, first and last in sample queue; water blank before samples)	85-115% of known value (After helium blank at first of analysis queue, before helium blank at end of sample set, and every 15 samples)	85-115% of known value (After first calibration check)	RPD≤20 (Every 15 samples)	NA
Metals (undigested)	RSKSOP-213v4	<QL for 80% of metals; (Beginning and end of each sample queue, 10-15 samples)	90-110% of known value (Beginning and end of each sample queue, 10-15 samples)	PE sample acceptance limits or 90-110% of known value (Immediately after first calibration check)	RPD<10 for 80% of metals; for results <5x QL, difference of ≤QL (Every 15 samples)	90-110% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals (digested)	RSKSOP-213v4	<10xMDL	See "undigested"	See "undigested"	RPD<20 for 80% of metals; for results <5x QL, difference of ≤QL (Every 15 samples)	80-120% Rec. for 80% of metals w/ no individual exceeding 50-150% Rec. (one per sample set, 10-15 samples)
Metals (undigested)	RSKSOP-257v3 and -332v0	<QL for 80% of metals; none>10xMDL (Beginning and	90-110% of known value (Beginning and end of	PE sample acceptance limits or 90-110% of	RPD<10 for 80% of metals for metals	90-110% Rec. for 80% of metals w/

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		end of each sample queue, 10-15 samples)	each sample queue, 10-15 samples)	known value (Immediately after first calibration check)	>5xQL (Every 15 samples)	no individual exceeding 70-130% (one per sample set, 10-15 samples)
Metals (digested)	RSKSOP-257v3 and -332v0	<ICP MDL for RSKSOP-213v4	See "undigested"	See "undigested"	RPD<20* for 80% of metals above 5xQL; for results <5x QL, difference of \leq QL (Every 15 samples) *35 for solids	80-120% average rec. with at least 50% of individuals within 50-150% rec. for pre-digestions and 70-130% rec. for all results for post-digestions (one per sample set, 10-15 samples)
SO ₄ , Cl, F, Br	RSKSOP-276v3	<MDL (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 15 samples)	80-120% Rec. (one per every 20 samples)
NO ₃ + NO ₂ , NH ₄	RSKSOP-214v5	<1/2 lowest calib. std. (Beginning and end of each sample queue)	90-110% Rec. (Beginning, end, and every 10 samples)	PE sample acceptance limits (One per sample set)	RPD<10 (every 10 samples)	80-120% Rec. (one per every 20 samples)
DIC/DOC	RSKSOP-330v0	<1/2QL (after initial calib., every 10-15 samples, and at end)	80-120% of known value (after initial calib., every 10-15 samples, and at end)	80-120% of known value (Immediately after calibration)	RPD<10 (every 15 samples)	80-120% Rec. (one per 20 or every set)

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Volatile organic compounds (VOC)**	RSKSOP-299v1	<MDL (Beginning and end of each sample set)	80-120% Rec. (Beginning, end, and every 20 samples)	80-120% of known value (Once at beginning)	RPD<20 (every 20 samples)	70-130% Rec. (every 20 samples)
Low Molecular Weight Acids	RSKSOP-112v6	<MDL (Beginning of a sample queue; every 10 samples; and end of sample queue)	85-115% of the recovery (Prior to sample analysis; every 10 samples; end of sample queue)	85-115% of recovery (Prior to sample analysis)	< 15 RPD (Every 20 samples through a sample queue)	80-120 % recovery (Every 20 samples through a sample queue)

This table only provides a summary; SOPs should be consulted for greater detail.

**Surrogate compounds spiked at 100 ug/L: p-bromofluorobenzene and 1,2-dichlorobenzene-d4, 85-115% recovery.

Corrective actions are outlined in the SOPs.

MDL = Method Detection Limit

QL = Quantitation Limit

PE = Performance Evaluation

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Table 14. Region VIII Laboratory QA/QC Requirements for Semivolatiles, GRO, DRO.

QC Type	Semivolatiles	DRO	GRO	Frequency
Method Blanks	<RL Preparation or Method Blank, one with each set of extraction groups. Calibration Blanks are also analyzed	<RL Preparation or Method Blank	<RL Preparation or Method Blank and IBL	At least one per sample set
Surrogate Spikes	Limits based upon DoD statistical study (rounded to 0 or 5) for the target compound analyses.	60-140% of expected value	70-130% of expected value	Every field and QC sample
Internal Standards Verification.	Every sample, EICP area within -50% to +100% of last ICV or first CCV.	NA	NA	Every field and QC sample
Initial multilevel calibration	ICAL: minimum of 6 levels (.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, $r^2 \geq 0.990$	ICAL: 10-500 ug/L RSD≤20% or $r^2 \geq 0.990$	ICAL: .25-12.5 ug/L for gasoline (different range for other compounds) RSD≤20% or $r^2 \geq 0.990$	As required (not daily if pass ICV)
Initial and Continuing Calibration Checks	80-120% of expected value	80-120% of expected value	80-120% of expected value	At beginning of sample set, every tenth sample, and end of sample set
Second Source Standards	ICV1 70-130% of expected value	ICV1 80-120% of expected value	ICVs 80-120% of expected value	Each time calibration performed
Laboratory Control Samples (LCS)	Statistical Limits from DoD LCS Study (rounded to 0 or 5) or if SRM is used based on those certified limits	Use an SRM: Values of all analytes in the LCS should be within the	Use and SRM: Values of all analytes in the LCS should be within the limits determined by the supplier. Otherwise 70-130%	One per analytical batch or every 20 samples, whichever is greater

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		limits determined by the supplier. Otherwise 70-130% of expected value	of expected value	
Matrix Spikes (MS)	Same as LCS	Same as LCS	70-130% of expected value	One per sample set or every 20 samples, whichever is more frequent
MS/MSD	% Recovery same as MS RPD ≤ 30	% Recovery same as MS RPD ≤ 25	% Recovery same as MS RPD ≤ 25	One per sample set or every 20 samples, whichever is more frequent
Reporting Limits*	0.1 µg/L (generally) ¹ for target compounds HF special compounds are higher	20 µg/L ¹	20 µg/L ²	NA

¹Based on 1000 mL sample to 1 mL extract

²Based on a 5 mL purge

*see QAPP Table 12

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Table 15. Region III Detection and Reporting limits for glycols.

Analyte [†]	Detection Limit ($\mu\text{g L}^{-1}$) [†]	Reporting Limit ($\mu\text{g L}^{-1}$) [†]
2-butoxyethanol	NA	NA
diethylene glycol	NA	NA
triethylene glycol	NA	NA
tetraethylene glycol	NA	NA

[†] Detection and reporting limits are still being determined, most will be between 10 and 50 pbb.

[‡] The samples are analyzed according to OASQA On Demand Procedures- See the Region 3 Laboratory QA manual for procedures. See Section 13.1.4.2 Procedure for Demonstration of Capability for "On-Demand" Data (Metzger et al., 2011)

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Table 16. USGS laboratory QA/QC requirements for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis using TIMS*.

QC Type	Performance Criteria	Frequency
Blanks	<1 ng per analysis	One per month during period of sample analyses. An unacceptable blank disqualifies all analyses back to previous acceptable blank.
Initial and Continuing Calibration Checks using USGS laboratory standard EN-1** ("operational" checks)	The value is expected to repeat to ± 0.003 percent (3 sigma) in replicate analyses of the $^{87}\text{Sr}/^{86}\text{Sr}$.	EN-1 is analyzed once for every 10 analyses of unknowns or more frequently.
Lab Duplicates	In a given suite of samples, any "unexpected" values are automatically repeated.	Blind duplicates are analyzed every 15 to 20 samples.

*Thermal Ionization Mass Spectrometry

**Internal standard EN-1 (contained Sr is that of modern sea water)

Corrective Actions: If any samples are affected by failure of a QC sample to meet its performance criteria, the problem shall be corrected and samples will be re-analyzed. If re-analysis is not possible (such as lack of sample volume), the data will be qualified with a determination as to impact on the sample data.

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Table 17. Supplies or consumables needed not listed in SOPs*

Item	Vendor	Part Number
Buffer Solution, pH 4	Fisher Scientific	SB101-500
Buffer Solution, pH 7	Fisher Scientific	SB108-500
Buffer Solution, pH 10	Fisher Scientific	SB115-500
Conductivity Standard, 1413µmho	Fisher Scientific	15-077-951
Zobell Solution	Fisher Scientific	15-176-222
Oakton DO Probe Membranes	Fisher Scientific	15-500-039
Bromcresol Green-Methyl Red Indicator	HACH	94399
Sulfuric Acid Cartridges, 0.1600N	HACH	1438801
Sulfuric Acid Cartridges, 1.600N	HACH	1438901
Delivery Tubes for Digital Titrator	HACH	1720500
Iron, Ferrous Reagent	HACH	103769
Sulfide 1 Reagent	HACH	181632
Sulfide 2 Reagent	HACH	181732
POL DO cap Membrane Kit/ Electrolyte Solution	YSI	605307
Silicone Tubing, size 24	Fondriest Environmental	77050009
Silicone Tubing, size 36	Fondriest Environmental	77050011
Polyethylene Tubing 0.25" ID x 0.375" OD	Fondriest Environmental	77050502
Polyethylene Tubing 0.375" ID x 0.50" OD	Fondriest Environmental	77050503
De-ionized Water	Varies	N/A
Distilled Water	Varies	N/A

* Equivalent products from other vendors can be used if needed.

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7.0 Figures

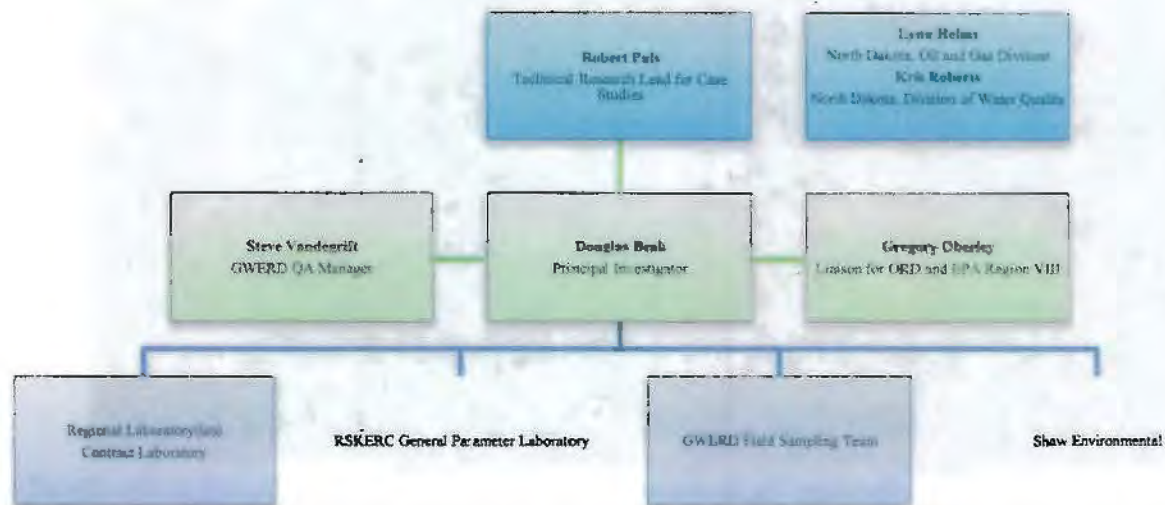


Figure 1. Organizational chart for the Hydraulic Fracturing Retrospective Case Study, Bakkan Shale, Killdeer and Dunn County, ND

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Figure 2. Aerial view showing the location of the Franchuk 44-20SHW well to the city of Killdeer, North Dakota and the surrounding area.

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Figure 3. A higher resolution aerial view of the Franchuk 44-20SWH well and surrounding area.

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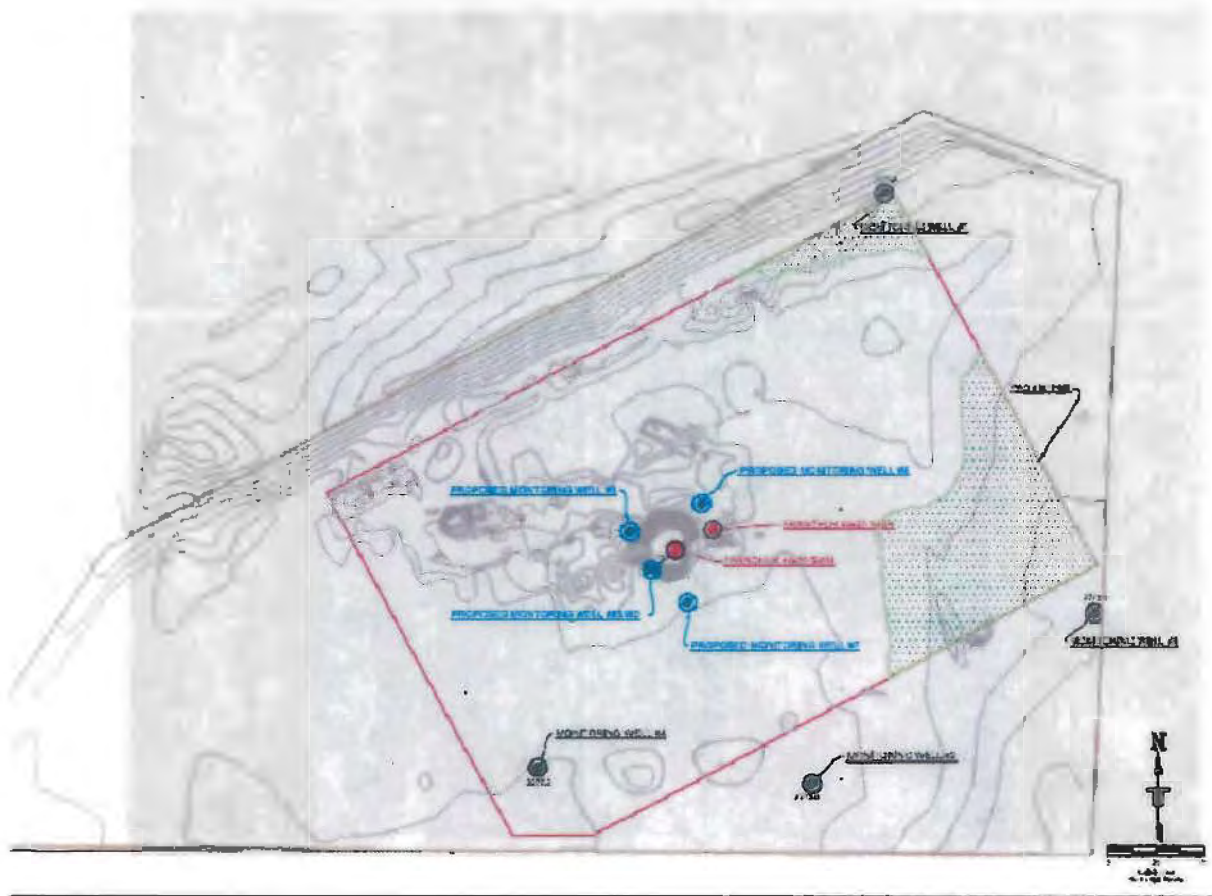


Figure 4. Locations of Monitoring well network for the Franchuk 44-20SWH well. The wells identified as proposed have been installed. Information was provided by the North Dakota Department of Health, Division of Water Quality, Terracon Consultants, and Denbury Onshore, LLC.

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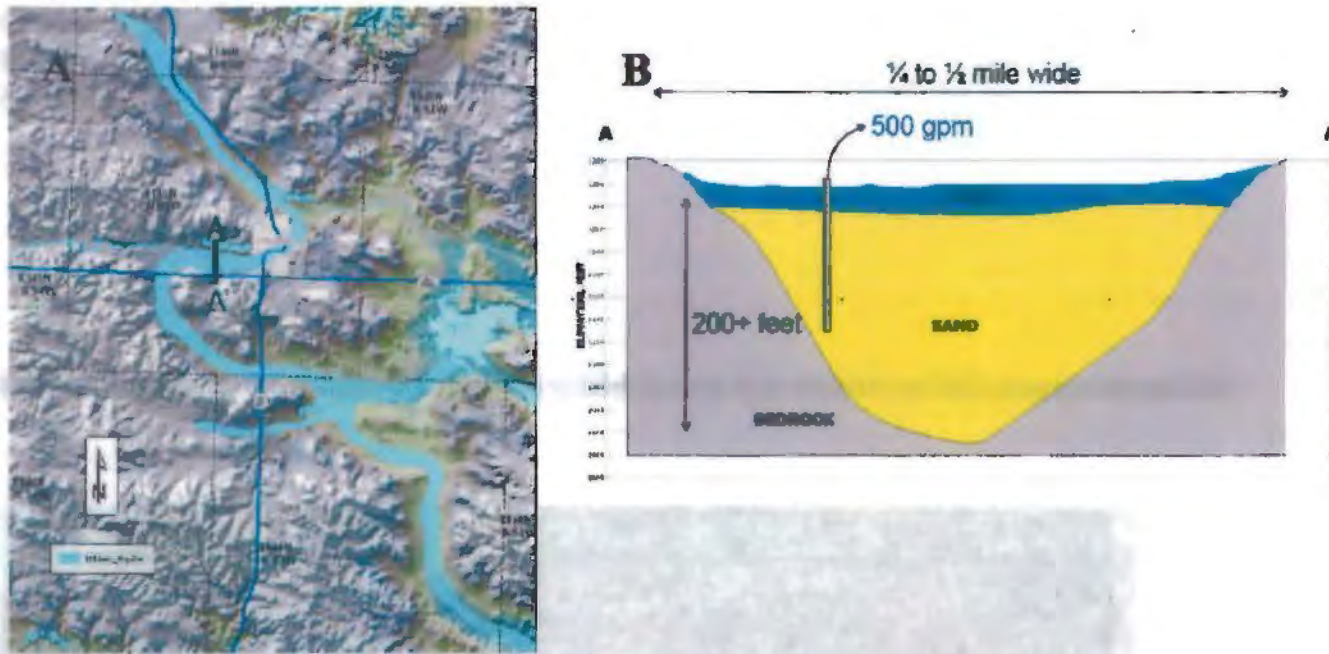


Figure 5. Map showing (A) the extent of the Killdeer Aquifer in Dunn County, North Dakota and (B) a geologic cross section of the Killdeer Aquifer (Shaver, 2009).

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Figure 6. Example of sampling a municipal supply well and municipal supply well sampling tap.

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Figure 7. Water supply well and sampling insert.

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Figure 8. North Dakota Water Commission well sampling and bladder pump controller.

Sample Analysis Request
and

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[illegible]

Figure 9. Chain of Custody form for submittal of water samples to laboratories.

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APPENDIX A

Isotope Support for the EPA Hydraulic Fracturing Study by the U.S. Geological Survey (USGS) Denver CO

Background: Strontium is an alkaline earth element that closely follows calcium in the geochemical and biological cycles. The critical parameter is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio which can be determined to a high degree of precision by thermal ionization mass spectrometry (TIMS). ^{86}Sr is a stable isotope of strontium whereas some of the ^{87}Sr is radiogenic from the decay of ^{87}Rb . In hydrologic studies, Sr isotopes are used to study (1) mixing of waters, (2) groundwater evolution due to water-rock interaction, (3) isotopic characterization of aquifers, and (4) weathering including the impact of climate change and acid rain. Numerous examples of each of these are available in the scientific literature. The addition of Sr isotopes to dissolved ion, trace metal, and other isotopic analyses (e.g., O and H) provides a powerful combination for addressing critical hydrologic and hydrochemical problems as shown by the selected references.

USGS Capability: Researchers in USGS isotope laboratories have been analyzing Sr isotopes for nearly a half century with ever increasing precision as instrumentation continually improves. The laboratory in Denver has two state-of-the-art TIMS and clean laboratories for these analyses. During the past 20 years, the USGS Geochemistry Team has worked on the Yucca Mountain Project under a stringent Quality Assurance/Quality Control program, and the team continues to use the DOE-approved technical procedures (attached).

Application to Hydraulic Fracturing Study: Formation water is typically many times more saline than fresh water and commonly more saline than ocean water. When hydraulic fracturing fluids are injected into rock units, it mixes with the formation water, and the flowback water typically has a high salinity. Potential contamination of groundwater can occur from the injection water which commonly contains a number of proprietary chemical compounds and flowback water which is a mixture of injection water and formation water. Use of Sr isotopes to detect contamination associated with the hydraulic fracturing process requires samples of (1) uncontaminated groundwater, (2) hydrofracing water, and (3) flowback water.

Scope and Cost of Analyses: Depending on the isotopic variability of the three water types, we anticipate that several tens of samples would be required for each site study. The cost of \$575 per sample will include the following:

- 1 A high precision $^{87}\text{Sr}/^{86}\text{Sr}$ analysis with a 2-sigma uncertainty of ± 0.00002 .
- 2 ICPMS analysis of Sr concentration (coefficient of variation of ± 5 percent).

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3 Sr isotope measurements of USGS standard EN-1 which is analyzed every six samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ values for EN-1 allow precise interlaboratory comparisons of analyses. These data will be compiled and included in the report.

4 For each study site, a report describing the isotopic results and their implications can be prepared.

5 Other isotopes (O, H, C, U, Pb) and other dissolved ions and trace metal concentrations can be determined by the USGS laboratories in Denver if needed.

6 USGS personnel can participate or advise in the specific site studies and sample collection if needed by the EPA.

Brenot, A., Baran, N., Petelet-Giraud, E., Negrel, P., 2008, Interaction between different water bodies in a small catchment in the Paris Basin (Breville, France): Tracing multiple Sr sources through Sr isotopes coupled with Mg/Sr and Ca/Sr ratios: *Applied Geochemistry*, v. 23, p. 58-75.

Brinck, E. L., and C. D. Frost, 2007a, Detecting infiltration and impacts of introduced water using strontium isotopes: *Ground Water*, v. 45, p. 554– 568.

Frost, C.D., and Toner, R.N., 2004, Strontium isotopic identification of water-rock interaction and groundwater mixing: *Ground Water*, v. 42, p. 418–432.

Gosselin, D.C., Harvey, F. Edwin, Frost, Carol, Stotler, Randy, Macfarlane, P. Allen, 2004, Strontium isotope geochemistry of groundwater in the central part of the Dakota (Great Plains) aquifer, USA: *Applied Geochemistry*, v. 19, 359-357.

Moller, P., Seise, S.M., Tesmer, M., Dulski, P., Pekdeger, A., Bayer, U., and Magri, F. 2008, Salinization of groundwater in the North German Basin: Results from conjoint investigation of major, trace element and multi-isotope distribution: *International Journal of Earth Science (Geol Rundsch)*, v. 97, p. 1057-1073.

Naftz, D.L., Peterman, Z.E., Spangler, L.E. 1997, Using $\delta^{87}\text{Sr}$ to identify sources of salinity to a freshwater aquifer, Greater Aneth Oil Field, Utah, USA: *Chemical Geology*, v. 141, p. 195-209.

Peterman, Zell E., and Wallin, Bill, 1999, Synopsis of strontium isotope variations in groundwater at Äspö, southern Sweden: *Applied Geochemistry*, v. 14, p. 939-951.

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Quattrocchi, F., Barbieri, M., Bencini, R., Cinti, D., Durocher, K., Galli, G., Pizzino, L., Shevalier, M., and Voltorni, N., 2006, Strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) chemistry in produced oil field waters: The IEA CO₂ monitoring and storage project: Advance in the Geological Storage of Carbon Dioxide, Springer, The Netherlands, p. 243-259.

Shand, P., Darbyshire, D.P.F., Love, A.J., Edmunds, W.M., 2009, Sr isotopes in natural waters: Applications to source characterisation and water-rock interaction in contrasting landscapes. Applied Geochemistry v. 24, p.574-586

Singleton, M.J., Maher, K., DePaolo, D.J., Conrad, M.E., and Dresel, P.E., 2006, Dissolution rates and vadose zone drainage from strontium isotope measurements of groundwater in the Pasco Basin, WA unconfined aquifer: Journal of Hydrology, v.321, p. 39-58.

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YMPB USGS TECHNICAL PROCEDURE

Rb-Sr Isotope Geochemistry

1. INTRODUCTION. This technical procedure describes the application and use of the Rb-Sr isotope system as a geochronometer and as a tracer of geologic processes and materials including rocks, minerals, water, and various man-made materials that contain Sr. This procedure applies to all U.S. Geological Survey (USGS), Yucca Mountain Project Branch (YMPB) and support personnel who perform these quality-affecting activities in support of the Office of Civilian Radioactive Waste Management (OCRWM) program.

Work initiated in accordance with procedures superseded by this technical procedure will be completed in accordance with this technical procedure. There is no impact to previous activities as a result of this new procedure. Modifications to this procedure shall be processed in accordance with YMPB-USGS-QMP-5.01, Preparation of Technical Procedures.

The utility of the Rb-Sr decay system in geochronology and isotope tracer studies is described by Faure (1986). ^{87}Rb decays to ^{87}Sr with a half-life of 48.8 billion years, and the change in isotopic composition of Sr (measured as $^{87}\text{Sr}/^{86}\text{Sr}$ where ^{86}Sr is a nonradiogenic isotope) is a function of the time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of the host environment. Geochemically, Rb is an alkali metal that closely follows K, and Sr is an alkaline-earth element with close affinities to Ca.

One form of the basic decay equation follows:

$$(^{87}\text{Sr}/^{86}\text{Sr})_p = (^{87}\text{Sr}/^{86}\text{Sr})_i + (^{87}\text{Rb}/^{86}\text{Sr})_p * (e^{\lambda t} - 1)$$

Where subscripts "p" and "i" refer to "present-day" and "initial", respectively; "t" is time in years; and λ is the decay constant for ^{87}Rb ($1.42 \times 10^{-11} \text{yr}^{-1}$).

For geochronologic applications, the above equation is solved for "t" which is the interval of time since the rock or mineral system formed with an initial Sr isotopic composition of $(^{87}\text{Sr}/^{86}\text{Sr})_i$ assuming closed system evolution (i.e. no loss or gain of parent or daughter isotopes other than by radioactive decay). For tracer studies, the above decay equation may or may not be relevant. Initial Sr isotope values $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values for igneous rock are valuable for characterizing the sources of magmas from which the rocks formed including possible assimilation of crustal rocks during ascent of the magmas. For this usage, the age of the system and the $(^{87}\text{Rb}/^{86}\text{Sr})_p$ must be known so that $(^{87}\text{Sr}/^{86}\text{Sr})_p$ can be corrected for the ingrowth of

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radiogenic ^{87}Sr . Other materials for which Sr isotopes can be effectively used as tracers or for characterization include calcite deposits such as in veins or calcretes, marine and terrestrial limestones; subsurface and surface waters and other waters such as may occur in a tunnel environment; and other Sr-Ca bearing materials, including cement/concrete and conveyor belts where the isotope ratios are used simply for baseline characterization of materials that may be introduced into a repository and subsequently impact other materials such as dust and condensate.

2. RESPONSIBILITIES.

2.1 Principal Investigator is responsible for assuring compliance with this procedure and for conducting the activities described in this procedure.

2.2 YMPB and Support Personnel are responsible for conducting the activities described in this procedure.

3. **INTERFACES.** The USGS may receive samples from the YMP Sample Management Facility following procedures for sample transmittal and control.

4. **TECHNICAL REQUIREMENTS.** Technical requirements of applicable planning documents associated with Rb-Sr Isotope Geochemistry are met through the implementation of this procedure. There are no other technical requirements.

5. **ASSOCIATED WORK ACTIVITIES.** Other work activities and procedures associated with implementation of this procedure include:

- YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*
- YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*
- YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*

6. **METHODS.** The general principles of isotope-dilution techniques are described by Faure (1986). Procedures described herein for the analyses of rock samples in the Rb-Sr laboratory (Denver, Colorado) are similar to those summarized by Peterman and others (1985). Adaptations of these methods are readily made for other materials. The use of high-purity reagents with

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certifications and ultra-high purity water (18×10^6 ohms resistivity, hereafter referred to as UHP water) facilitates maintenance of a low-blank environment.

6.1 Methods:

6.1.1 Sample Collection and Preparation: Samples analyzed under this procedure will be collected and controlled in compliance with YMPB-USGS-QMP-SII.01, R0 (Identification and Control of Samples). Standard thin sections may be used for preliminary determination of mineralogic composition of some samples. Samples of rock are crushed in a laboratory jaw crusher to particle sizes of 1.0 cm or less. Approximately 100 grams of this material are further reduced to approximately 200 mesh size by pulverizing in a shatterbox using a hardened steel grinding container. To prevent cross contamination among samples, the crushing equipment is cleaned thoroughly between samples by washing and scrubbing using stainless steel brushes.

Other methods of sample preparation including hand picking of grains, can be used as required by the problem and the nature of the samples. For some samples, an approximate 3-gram split of the rock powder can be analyzed for K, Ca, Ti, Rb, Sr, Y, Zr, Nb, La, Ce, and Ba on an energy dispersive X-ray fluorescence (XRF) unit preparatory to isotope dilution analyses in accordance with YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*.

6.1.2 Chemical Dissolution: Rb and Sr must be liberated from the host material and isolated from potentially interfering elements for isotopic analyses. The type of material dictates the method of dissolution as described below:

6.1.2.1 Silicate Samples: A few tens to hundreds of milligrams) of silicate powder is weighed for dissolution. A measured amount of Rb and Sr spike solution may be added if isotope-dilution concentrations are required. The spikes consist of known concentration of ^{84}Sr and ^{87}Rb . Sample dissolution is accomplished through a combination of small amounts of concentrated H_2SO_4 , HCl , HClO_4 , or HNO_3 with concentrated HF . After refluxing on a hot plate to dryness the resultant precipitate is brought into solution with HCl or HNO_3 and centrifuged. The supernatant solution is pipetted in small volumes onto an ion-exchange resin column pretreated with HCl or HNO_3 . After washing with a measured volume of HCl or HNO_3 acid, the final solution containing the purified Sr is collected in a Teflon beaker and dried on low heat. The sample is transferred to the mass spectrometer laboratory for isotopic analysis.

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Alternatively, Rb and Sr concentrations can be determined by ICP-MS, according to YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*.

6.1.2.2 Carbonate Samples: Carbonate samples are typically weighed and dissolved in weak HCl or HNO₃ leaving admixed silicates intact. Other methods of leaching include, but are not limited to 10 percent CH₃COOH (acetic acid), or 10 percent disodium EDTA (ethylenedinitrilotetraacetate). For isotope dilution determination, a weighed amount of Sr spike is added to the sample before dissolution. The leachate is separated from the insoluble material by centrifuging and the supernatant liquid is transferred to separate container. After drying the leachate with low heat, the residual is dissolved in a small amount of HNO₃ acid. To estimate the proportion of carbonate in the original sample, the acid-leached residue is washed with ultra high purity (UHP) H₂O, dried and weighed. Ion exchange procedures to isolate Sr from the solution are similar to those described above in Para. 6.1.2.1 for the silicate samples.

6.1.2.3 Water Samples: Water samples are weighed and spiked with Sr isotope (if necessary) then evaporated to dryness in Pyrex or Teflon beakers in an environmental hood. The dried sample is brought up in HNO₃ and centrifuged. A portion of sample solution may be prepared for trace element concentration determination by ICP MS in accordance with YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*. Sr is isolated by ion-exchange methods, following the procedures in Para. 6.1.2.1.

6.1.3 Mass Spectrometry: Isotopic analyses of Rb and Sr will be done by thermal ionization mass spectrometry (TIMS). A drop of 1.0N HCl is added to the Sr sample (0.1-5 micrograms of Sr), which was prepared as described above in section. 6.1.2. Prior to loading any solutions the rhenium or tantalum filaments used will be outgassed in a vacuum to remove impurities. The Sr sample is dried on the filaments by passing a low current (1.5-2.0 amps) through the filaments. The rhenium sample filaments are configured with an ionizing filament and placed sample turret of the mass spectrometer. Tantalum filaments are used for single filament runs. Following pump down to a source pressure of approximately 4×10^{-7} mm of Hg, an ion beam is generated by heating the sample filaments with the ionizing filament operating at approximately 1.8×10^3 C. When a stable Sr beam of approximately 0.5-5 volts of ⁸⁸Sr is attained, data collection is started. Five or more blocks of data are to be taken until an average ⁸⁷Sr/⁸⁶Sr value with an uncertainty (95 percent confidence level on the mean) of 0.0001 is attained. The

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measured ratios will be corrected for mass discrimination by normalizing the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio to a value of 0.11940 and adjusting the other ratios accordingly.

Rb will also be loaded onto a rhenium sample filaments, configured with an ionizing filament, and installed on the source of the Rb mass spectrometer. Operate the ionizing filament at a lower temperature (approximately 1.5×10^3 C) than that for Sr. Generally three to five blocks of data will yield a suitable mean value with <0.03 percent variation.

The Sr and Rb isotopic ratios will be combined with data on samples and spike weights to calculate Rb and Sr contents, and $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

6.2 Materials and Equipment: Materials and equipment needed to perform this work include:

6.2.1 Sample Preparation:

- Standard thin sections (For indication only)
- Laboratory jaw crusher
- Spex Shatterbox
- Stainless steel brushes
- Kevex energy dispersive X-ray fluorescence unit (For indication only)
- Steel mortar and pestle
- Microscope for hand picking

6.2.2 Chemical Dissolution:

- Ultra-high purity (UPH) H₂O (18.2×10^6 ohms resistivity)
- Ultrex, Baker Analyzed, C Star Suprapur (EM Science) and/or reagents of equivalent or higher purity of the following: H₂SO₄ (concentrated) HF (concentrated) HClO₄ (concentrated) HNO₃ (concentrated) HCl (concentrated) CH₃COOH (acetic acid) Disodium EDTA (ethylenedinitrilotetraacetate)
- Platinum dishes
- Teflon covers, jars, beakers, tubes and other equipment
- Electronic analytical balance
- NIST traceable weights
- ^{87}Rb spike solution
- NIST SRM-607 Rb standard
- ^{84}Sr spike solution
- NIST SRM-610 or 611 Sr standard

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- Hot plate
- Centrifuge
- Ion-exchange resins and columns
- Parafilm
- Environmental hood or laminaire flow hoods
- Appropriate standard laboratory equipment including, but not limited to: quartz, Teflon, and Pyrex beakers; graduated cylinders; and glass and plastic centrifuge tubes (accuracies in all ranges to ± 5 percent)
- NIST glass and rock standards such as, but not limited to, SRM-610, SRM-611 and SRM-987 for strontium and SRM-607 for rubidium.

6.2.3 Mass Spectrometry: Including, but not limited to a thermal ionization mass spectrometer (TIMS) e.g. Finnigan MAT 262 and Thermo Elemental Triton; and an inductively coupled plasma (ICP) mass spectrometer e.g. Thermo Elemental PQ-3:

- Rhenium ribbon
- Tantalum ribbon
- EN-1 standard carbonate
- Biotite or K-feldspar mineral samples
- NIST SRM-987 (for strontium)
- NIST SRM-727 (for rubidium)
- BCR-1 standard rock sample
- High purity elemental standard solutions
- NIST 1643 and 1640 water standards
- Liquid N₂

Collected data will be traceable to the M&TE used to collect that data by lab notebooks and computer printouts from the mass spectrometer.

Special handling of equipment is required, e.g., protective gloves, when appropriate.

6.3 Operational checks: Operational checks will be used to determine if equipment is operational and capable of providing acceptable data. Results of an operational check are acceptable by monitoring the mass spectrometer results.

6.3.1 Chemistry Laboratory/Mass Spectrometer: Evaluation of the effectiveness of the chemistry laboratory procedures is achieved primarily by monitoring the mass spectrometer results on accepted standard materials.

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Standard materials include, but are not limited to NIST glass and rock standards such as SRM-610, SRM-611, and SRM-987 for strontium or SRM-607 for rubidium. Operational checks on the mass spectrometers are performed at least every 30 samples or as necessary by analyzing a laboratory standard material. For Sr the laboratory standard is calcium carbonate prepared from a modern *tridacna* (giant clam) shell collected from Enewetok Lagoon and designated EN-1. Sr in the clam shell represents the isotopic composition of modern sea water. Because the $^{87}\text{Rb}/^{85}\text{Rb}$ ratio is constant in nature, rubidium isotopic measurements are checked by analyzing Rb from an unspiked biotite or K-feldspar. These operational checks of the chemistry and mass spectrometry laboratories shall incorporate components that measure and/or regulate volume, vacuum, filament current/temperature, accelerating voltage, and ion-beam current. If the results of these operational checks are not within acceptable limits per Para. 11 of this procedure, mass spectrometer and/or laboratory operations are suspended until the problem(s) is (are) identified and rectified. If elemental concentrations of the standards indicate a significant change in the spike solution concentration then the affected spikes are re-determined with NIST standards. These checks will be documented in the mass spectrometer logbook.

6.3.2 Analytical Balance: An operational check of the analytical balance will be performed periodically using class 1 weights, which are traceable to NIST certification. Annual calibration will be performed in accordance with YMPB USGS GCP-42, Calibration of Laboratory Scales and Analytical Balances. Operational checks will be documented in a lab notebook.

7. PREREQUISITES, LIMITS, PRECAUTIONS, AND ENVIRONMENTAL CONDITIONS.

7.1 Prerequisites: There are no special prerequisites or precautions associated with the implementation of this procedure. Although a clean area (e.g. HEPA filtered) is necessary for chemistry operations.

7.2 Limits: Mass spectrometers are complex systems composed of a number of sensitive electronic components. Any electronic problem will commonly manifest itself as beam instability during the course of an analysis. This is identified immediately by the operator on the basis of an unstable signal. The instruments will be shut down until the problem is rectified. There are no unconstrained assumptions in the laboratory procedures that have not been experimentally tested during the long-term operation of the facility.

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7.3 Precautions: Besides the usual laboratory safety equipment there are no special precautions associated with the implementation of this procedure.

7.4 Environmental Conditions: Water samples should be processed in an environmental hood.

8. **ACCEPTANCE CRITERIA.** The satisfactory performance of this procedure can be judged by the quantitative replicate analyses of NIST-certified standard samples. Isotope dilution measurements will be accurate to 1 percent of their values (2 sigma) or better. Measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ will be accurate to 0.015 percent or better. Total laboratory blanks for Rb and Sr will be determined as necessary, and these shall be below 10 nanograms for the data to be accepted. 8.1 Unless otherwise stated, the precision needed for all measurements specified in this procedure is 5 in the last significant figure. Volume and temperature measurements within the chemical dissolution process and measurements of vacuum, filament current/temperature and accelerating voltage within the mass spectrometry analysis are approximate and absolute determination of these parameters is not necessary for successful performance of the analysis. Approximate numbers are provided within this procedure to ensure consistency between samples and standards tested. These measurement parameters are encompassed within the operational checks of the chemistry/mass spectrometry procedures where proper operation of the system is validated by testing standards of known characteristics.

9. **SAMPLES.** Samples are handled as part of this procedure and shall be identified and controlled in accordance with YMPB-USGS-QMP-SII.01, *Identification and Control of Samples*.

9.1 Identification and Traceability: Samples shall be controlled and tracked in compliance with YMPB-USGS-QMP-SII.01, R0, *Identification and Control of Samples*.

9.2 Control, Storage, and Disposition: Samples shall reside in the custody of the PI, or delegate, who shall store them in a secured area at the Denver Federal Center, Denver, Colorado. Final disposition of individual samples, including transfer to another YMP participant, disposal, or the need for archiving, shall be determined by the PI and shall be documented. Total consumption of a sample during analysis shall also be documented.

9.3 Special Treatment: No special handling, storage and/or shipping are required unless the PI designates the sample(s) as special. Special samples will be treated accordingly and documented.

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9.4 Nonconforming Samples: Nonconforming samples will be documented in accordance with YMPB-USGS-QMP-SII.01.

10. SOFTWARE. Software is used in this procedure are an integral part of the mass spectrometer equipment and is verified by system calibrations performed per the requirements of this procedure. Software used in this procedure will be controlled and documented in accordance with YMPB-USGS-QMP-SI.01, *Software Management*.

11. MEASURING AND TEST EQUIPMENT.

11.1 Calibration Requirements: Calibration of selected equipment is required. All calibrations will be performed and documented in accordance with YMPB-USGSQMP-12.01, *Control of Measuring and Test Equipment*, including application of calibration status stickers and reporting of out of calibration conditions. Measuring and test equipment (M&TE) that requires calibration include:

11.1.1 Mass Spectrometer(s): The mass spectrometer(s) is calibrated independently of the laboratory by analyzing the NIST standards SRM-987 (strontium) and/or SRM-727 (rubidium). These standards are salts of the elements and therefore do not require extensive laboratory preparation. These calibrations will be performed annually or as necessary.

11.1.2 NIST Traceable Weights: NIST traceable weights are calibrated every 5 years or as necessary by an OCRWM OQA approved/accepted supplier.

11.1.3 Analytical Balance: The laboratory scales and analytical balances are calibrated in accordance to YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*. Operational checks will be documented in a laboratory notebook.

12. CONSUMABLE STANDARDS/MATERIALS. Consumable materials will be purchased from an OCRWM approved vendor, or from a non-OCRWM vendor for which justification is documented and approved in accordance with YMPB-USGS-QMP-12.01. Each container or consumable will be labeled with shelf-life information and date. Use of consumable standards beyond the expiration dates is possible if the material quality can be verified by the PI or by an OCRWM approved verification plan. Comparison of consumable materials can be verified with the successful analysis of standards and sample materials. Standard materials include, but are not limited to, SRM-987, NBS-611 and other NIST traceable and internationally accepted USGS

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standard materials. Sr isotope standards do not change with time due to the long half-life of ^{87}Rb and shelf life is not applicable.

13. HANDLING, STORAGE AND SHIPPING OF EQUIPMENT AND CONSUMABLES.

No special handling, storage and/or shipping are required. All material and equipment shall be as per listed manufacturer or equivalent and will adhere to all federal, state, and local requirements. Equipment and consumable materials will be handled and stored in a manner consistent with USGS chemical safety policies. Use of acid-storage cabinets, secondary containment, personal protective equipment, and limited access practices will be used as appropriate. Bench-top chemistry is performed under HEPA-filtered air flow in temperature-controlled laboratories. Cleanliness of the labware, lab environment, and consumable reagents is monitored by routine inclusion of total-process blanks (pure spike solution that undergoes the entire chemical digestion and separation processes). No shipping of equipment or consumables is required.

14. ELECTRONIC MANAGEMENT OF INFORMATION. Data will not be released from the laboratory until all samples of a given set have been examined for internal coherence. Mass spectrometric measurements of isotopic ratios are obtained on hard copy as output from the instruments. The relevant ratios are transferred by data entry to electronic media and then retrieved from this media for double back-checking against the mass spectrometer records. Sample weights and spike weights are also entered into electronic media and then double-back checked against entries in the laboratory notebooks. All of the checking is done before the technical data submittal. The maintenance of security and integrity of any electronic data files shall be ensured by using password protected drives which are routinely backed up.

15. RECORDS. The following QA/QA records are submitted by the PI, or delegate, to the Records Processing Center through the Records Management Specialist in accordance with YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*: 15.1 Records Packages: The following may be submitted as part of a records package:

15.1.1 Data Records: The basic completed analytical data sets obtained will consist of the Rb and Sr contents (if applicable) and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples. These are obtained from the mass spectrometer analyses, the sample and spike weights, and the concentrations of the Rb and Sr spike solutions.

- Table of Sr Data
- Record of Mass Spectrometer Run
- Rb-Sr Sample Data Sheet (if appropriate)
- Copy of Calibration Certificates for Weight(s) (if appropriate)
- Copy of Mass Spectrometer Calibration sheet.

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- Copy of Inclusive Pages from Laboratory Notebook (pages with inclusive operational check dates, if appropriate)

15.1.2 Supporting Information:

- Calibration documentation identified in Para. 11.1 shall be submitted as supporting information.
- Chemistry laboratory notebooks shall record, at a minimum, sample identification and dates of analyses.
- Mass spectrometer logbooks shall record, at a minimum, sample numbers, dates analyzed, element analyzed, instrument identification, and instrument operator.
- Notebooks and logbooks contain supporting information and are not considered data unless specified so by the PI. If a notebook or logbook contains data, a statement will be noted in the book documenting which information is data. As appropriate, the documentation containing the information shall be submitted as part of the data records package identified in Para. 15.1.1.

Information obtained from the use of standard thin sections and the Kevex energy dispersive XRF unit is used in this procedure for indicative purposes only and does not affect the outcome and quality of the data acquired from the use of this procedure.

15.2 Individual Records: None

16. REFERENCES. References cited in this procedure are listed below.

- YMPB-USGS-QMP-5.01, *Preparation of Technical Procedures*
- YMPB-USGS-QMP-12.01, *Control of Measuring and Test Equipment*
- YMPB-USGS-QMP-17.01, *Quality Assurance Records Management*
- YMPB-USGS-QMP-SI.01, *Software Management*
- YMPB-USGS-QMP-SII.01, *Identification and Control of Samples*
- YMPB-USGS-GCP-25, *Determination of Chemical Composition by Energy Dispersive X-Ray Fluorescence Spectrometry*
- YMPB-USGS-GCP-38, *Determination of Chemical Composition by Inductively Coupled Plasma Mass Spectrometry*
- YMPB-USGS-GCP-42, *Calibration of Laboratory Scales and Analytical Balances*
- Faure, Gunter, 1986, *Principles of Isotope Geology*: John Wiley and Sons, New York, 589 p.
- Peterman, Z.E., Sims, P.K., Zartman, R.E., and Schulz, K.J., 1985, Middle Proterozoic uplift events in the Dunbar Dome of northeastern Wisconsin, USA: Contributions to Mineralogy and Petrology, v. 91, p. 138-150

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17. ATTACHMENTS. None.

18. HISTORY OF CHANGES.


<u>Revision/Modification No.</u>	<u>Effective Date</u>	<u>Description of Changes</u>
R0	5/14/2007	Initial issue.

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QA:QA

APPROVALS AND EFFECTIVE DATE.

EFFECTIVE DATE: 5-14-2007

CONCURRENCE:



Kiyoto Peta
Principal Investigator, Yucca Mountain Project Branch, USGS

5/7/2007


Date



Zell Peterman
Technical Reviewer, Yucca Mountain Project Branch, USGS

May 7, 2007

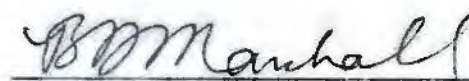
Date



Pamela A. Motyl
QA Manager, Yucca Mountain Project Branch, USGS

5/7/07

Date



Brian D. Marshall
Chief, Geochemistry Team, Yucca Mountain Project Branch, USGS

DM
5/7/07

5/8/07

Date

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Revision History

- Added $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes to analyte list
- Added O, H stable isotopes of water
- Added section for phased approach for case studies
- Revised sampling protocols for domestic wells, supply wells, and water commission wells
- Revised background information based on new information from Denbury
- Added USGS Laboratory contact information
- Revised Analysis of Data section
- Revised Assessment Results section- Reports will now be submitted to Technical Research Lead for Case Studies
- Revised Reports to Management section- Audit reports will be sent to Technical Research Lead for Case Studies
- Updated Reference section to include new references for isotopes and field parameters
- Updated Table 3, 8, and 11 to include current methods used
- Updated Table 9 to clarify Field QC samples needs
- Revised Table 13 to reflect QC sample frequencies
- Revised Table 14 to reflect new QC information provided by EPA R8 lab
- Added Table 16 for USGS QA/QC requirements
- Added Figure (Figure 6) to show sampling of municipal supply wells and sampling port
- Added Figure (Figure 7) to show sampling of water supply well and and sampling adaptor
- Added Figure (Figure 8) to show the sampling of ND Water Commission well using a portable bladder pump
- Added Appendix A for Sr isotope methodology used by USGS

